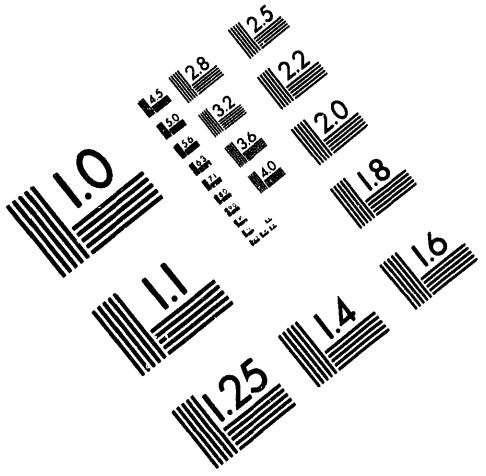

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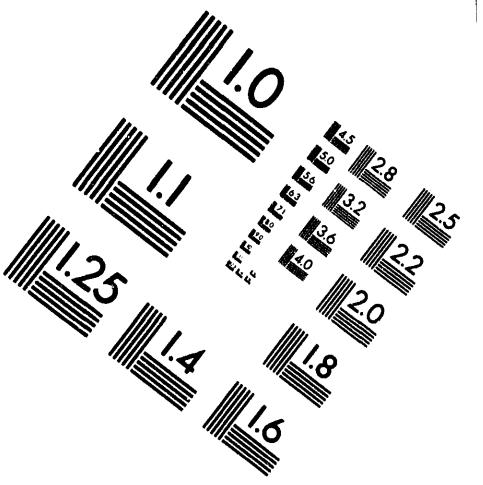

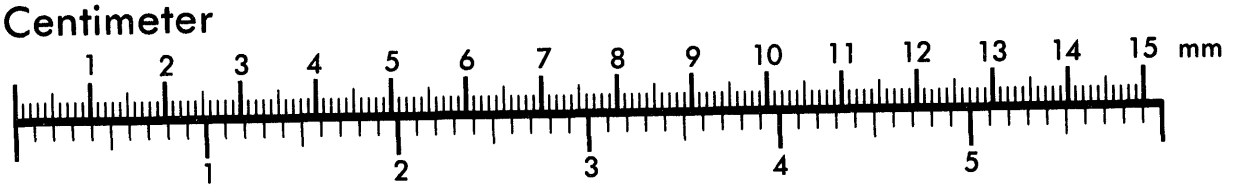

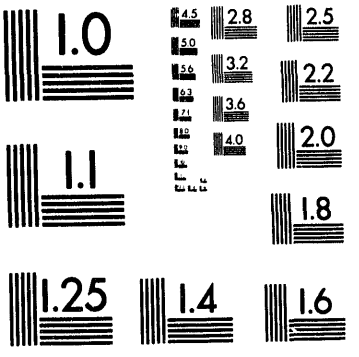

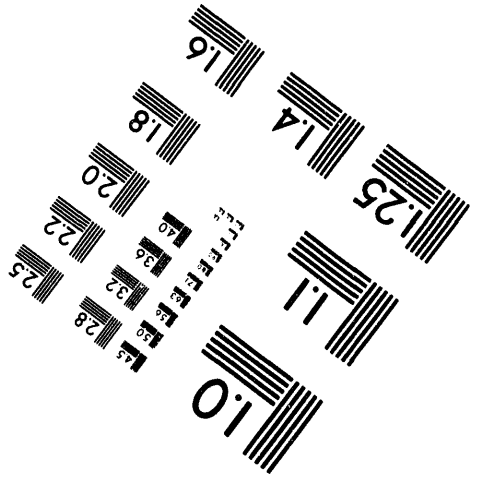

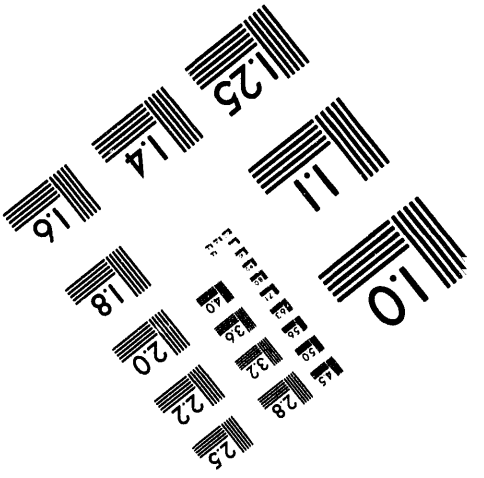

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MIXED WASTE

Proceedings of the Second International Symposium
Baltimore, Maryland, August 17 - 20, 1993

Edited by

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PREFACE

This volume contains the peer-reviewed and edited versions of papers submitted for presentation at the Second International Mixed Waste Symposium. Following the tradition of the First International Mixed Waste Symposium, these proceedings were prepared in advance of the meeting for distribution to symposium participants.

The symposium was organized by the Mixed Waste Committee of the American Society of Mechanical Engineers (ASME). Consistent with requirements of ASME, all papers were reviewed by three reviewers, of which at least two were members of ASME. The program committee was appointed by the ASME Mixed Waste Committee and consisted of the following individuals:

Nancy Rothermich, Martin Marietta Energy Systems, Chairperson
Gary Benda, Rust International
Dick Blauvelt, BDM
Debbie Browning, Rust International
Julie D'Ambrosia, EnviroTech
B. Mike Eisenhower, Battelle, Oak Ridge
Bob Fjeld, Clemson University
Bill Gregory, Foster Wheeler
Tim Harms, DOE HQ
Susie Jackson, Lawrence Livermore National Laboratory
Myron Kaczmarsky, Ebasco
Sheila Little, Fluor Daniel
Tom McLaughlin, Bovay Northwest
Lance Mezga, Martin Marietta Energy Systems
Alan Moghissi, Temple University
Colleen Owens, EG&G Idaho
Arlene Selber, Parsons Environmental
Dennis Skrincosky, STI

A. Alan Moghissi was the general chairman of the meeting with Leslie Wong and Gerri Wyer being responsible for day-to-day operation of the symposium.

During the Planning for publication of proceedings the organizers of the symposium faced two options. Many symposia require availability of the papers considerably before the date of the meeting. The available time can subsequently be used to thoroughly review the manuscripts and provide for extensive editing of the texts. Others choose to publish the manuscripts as submitted or with minimal review or editing. The latter approach permits the authors to present their latest findings. Neither one of these approaches appeared appealing. Instead an attempt was made to give the authors as much chance as possible to include the most up-to-date information in their papers. In order to avoid potential shortcomings of such an approach, an editorial support group was established at Temple University to manage the editorial process. This group was led by Betty Brown and included Vijaya Reddy Bynagari, Kuppuswamy Rajkumar, Peter Zandi, Leslie Wong, Tamika Barrett, Elaine Kravitz, Kamilah Meek, and Sharon Burdette.

A careful reader will find several shortcomings in these proceedings. For example, several authors did not follow instructions dealing with metric (SI) units. The authors were instructed to use entirely metric units, or if they used other units, they were to include metric equivalents. Unfortunately, certain authors chose to disregard these instructions. There was insufficient time to correct these errors.

During the editing process it became clear that the technical community had significant problems in referencing laws and regulations. Therefore, despite the best efforts of the editors and the editorial group,

a careful reader will find inconsistencies in referencing regulations. In the U.S., regulations may be referenced by one of two ways:

1. All regulations are published in the Federal Register, a publication of the U.S. government which is printed daily during the workdays of the week. These regulations may be referenced as U.S. Environmental Protection Agency, Land disposal restrictions "no migration" variances; proposed rule 40 CFR 268 and 271. Fed. Reg. 57, 35940-35954, 1992.

2. All regulations are published in the Code of Federal Regulations which is up-dated annually as of July 1 of every year. Therefore, a regulation may be cited U.S. Environmental Protection Agency, Identification and listing of hazardous waste, 40 CFR 261 U.S., Government Printing Office, Washington, D.C., (1992).

Unfortunately, it was not possible to go over every paper and correct the references. Therefore, the reader will find repeated references to regulations using a code such as 49 CFR 173 or 29 CFR 1900.

The regulations of concern to the readers of these proceedings are:

10	Department of Energy and Nuclear Regulatory Commission
29	Department of Labor including Occupational Safety and Health Administration
40	Environmental Protection Agency and Council of Environmental Quality
49	Department of Transportation

Therefore, 10 CFR 20 will deal with energy and 40 CFR 179 will contain regulations on transportation.

We are most grateful to those authors who followed instructions. They made our job significantly easier. We also appreciate the patience of the speakers who were called and asked to provide information with a day or so notice and had to comply with stringent editorial requirements. Finally, we believe the formation of ASME Mixed Waste Committee and the convening of the Second International Mixed Waste Symposium are indicative of the dedication of the technical community to solve a problem which is of environmental and societal concerns.

A. Alan Moghissi
Richard K. Blauvelt
Gary A. Benda
Nancy E. Rothermich

CHAPTER 1

Stabilization Technologies

THE NITRATE TO AMMONIA AND CERAMIC (NAC) PROCESS: A NEWLY DEVELOPED LOW-TEMPERATURE TECHNOLOGY

A. J. Mattus and D. D. Lee

Oak Ridge National Laboratory, Oak Ridge, TN

ABSTRACT. Bench-top feasibility studies with Hanford single-shell tank (SST) simulants, using a new low-temperature (50-60°C) process for converting nitrate to ammonia and ceramic, have conclusively shown that between 90 and 99% of the nitrate at Hanford can be readily converted to ammonia. In this process, aluminum powders or shot can be used to convert alkaline, nitrate-based supernate to ammonia and an alumina-silica-based ceramic solid. The process may actually be able to utilize already contaminated aluminum scrap metal from various U.S. Department of Energy sites to effect the conversion. The final nitrate-free ceramic product can be calcined, pressed, and sintered like any other ceramic. Based upon the starting volumes of 6.2 and 3.1 M sodium nitrate solution (probable supernate concentrations resulting from salt-cake/sludge removal from the Hanford SSTs), volume reductions as high as 70% are currently obtained, compared with an expected 40 to 50% volume increase if the Hanford supernate were grouted.

Engineering data extracted from bench-top studies indicate that the process will be very economical. These data were used to cost a batch facility with a production rate of 1200 kilograms of nitrate per hour for processing all the Hanford SST waste over 20 years. Our process cost analysis indicates that between $2.01 and 2.66 will be required to convert each kilogram of nitrate. Based upon 1957 literature, these costs are one-third to one-half of the processing costs quoted for electrolytic and thermal processes.

The ceramic waste form offers other cost savings associated with a smaller volume of waste as well as eliminates other process steps such as grouting. Silica added to the reactor, based upon the total sodium in the waste, permits us to actually bind the sodium in a nepheline phase of the final ceramic structure as well as bind most metals and nonmetals in the ceramic.

INTRODUCTION

Sodium nitrate–based wastes are common to many U.S. Department of Energy facilities throughout the United States. According to 1984 figures, more than 242,700 metric tons of nitrate wastes was stored at facilities such as the single-shell tanks (SSTs) at the Hanford, Washington, site; the Savannah River site; the Melton Valley Storage Tanks at ORNL; and the Pad A Waste at Idaho Falls. This study has been directed at a surrogate supernate representing solution resulting from dissolving and decanting the salt cake/sludge in the Hanford SSTs, of which there are 149 tanks with capacities of one million gallons each.

Wastes at the Hanford site can be subdivided into high level waste (HLW), transuranic (TRU), and low level waste (LLW), with the HLW and TRU wastes targeted for vitrification and the LLW targeted for immobilization in cement-based grout, although a final decision is not expected until 1996. The LLW contains most of the sodium nitrate and would be grouted in near-surface vaults, in a similar fashion to efforts at Savannah River using "salt stone."

Nitrate in groundwater can pose a serious threat to the health of the public. It is for this reason that the U.S. Environmental Protection Agency (EPA) has set the nitrate concentration limit in drinking water at 44 ppm as nitrate, or 10 ppm as monatomic nitrogen (N).

BACKGROUND AND CHEMISTRY

Aluminum is the third most abundant element in the earth's crust (8.1%), exceeded only by silicon and oxygen. Aluminum is not found in a free form in nature as a metal (placer form) as is the case for metals such as gold and silver. This is because aluminum is not thermodynamically stable in the presence of oxygen and quickly forms the oxide. The oxide coating, once formed, can allow the aluminum to exist for a useful length of time in the earth's atmosphere.

In an aqueous medium, especially one that is distinctly alkaline, the protective oxide is sparingly soluble. Upon abrasion or partial solubilization of the oxide, the metal dissolves by reducing the hydrogen component of water to gaseous hydrogen or reduces some other reducible species that may be present, such as nitrate or nitrite.

The free energy change associated with the oxidation of aluminum (-378 kcal/g-mol) to its most stable water-free oxide, alumina (Corundum), is quite large and exothermic. The thermodynamic driving force for aluminum metal to be oxidized or function as a strong reductant is also evidenced by the fact that aluminum is present in nature as alumina, in bauxite ore.

Interestingly, the nitrate reduction described in this paper is also a type of electrochemical process that is related to the Hall-Herault process, with which aluminum is produced today; the nitrate to ammonia and ceramic (NAC) process is actually the Hall-Herault process in reverse. Admittedly, a major difference is that the NAC process occurs in an alkaline, aqueous solution rather than in a water-free molten salt bath. The aluminum metal can be considered to be like a charged capacitor or battery, ready to release its energy during the reduction of nitrate to ammonia gas.

We can therefore take advantage of this source of stored electrons to reduce nitrate or nitrite ions to ammonia gas. The following standard reduction potentials, in aqueous solutions at 25°C, reveal how powerful a reductant aluminum metal is in alkaline solution:

$$Al(OH)_3 + 3e^- \rightarrow Al + 3OH^- \qquad E^\circ = -2.31\ V \tag{1}$$

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 \uparrow + 9OH^- \quad E^\circ = -0.16\ V \tag{2}$$

From the magnitude of the difference of the absolute values of these reduction potentials, it can be seen that aluminum is indeed more than capable of reducing nitrate to ammonia. In addition, aluminum can reduce water to form hydrogen gas and hydroxide in accordance with equation 3; this reaction lowers efficiency and produces unwanted hydrogen during the very last part of the reduction of nitrate, when the concentration is low (<3000 ppm).

$$2Al + 6H_2O \rightarrow 3H_2 \uparrow + 6OH^- + 2Al^{+3} \tag{3}$$

Although the above standard potentials are only for ideal solutions and conditions and the system is more complex than described, one can realize the order-of-magnitude differences involving thermodynamic driving forces for the reduction of nitrate and water. It is for this reason that this process using aluminum metal is able to work so well.

The calculated heat of reaction for the reduction of nitrate to ammonia and the conversion of aluminum metal to oxide is -381 kcal/mol of sodium nitrate. For this reason, an efficient cooling system must be an integral part of the reactor design. The heat of reaction is calculated based upon the free energy change between aluminum metal and its oxide and accounts for the major part of the overall free energy change of the reaction.

Formation of Reactor Product

Upon adding aluminum powder to a 50°C solution that is alkaline (pH >11.5) and that contains ~4 M sodium nitrate, one obtains an initial delay and then a reaction that is associated with a rapid increase in temperature. During the early stage of the reaction, the solution remains clear until, at some point, dense white gibbsite ($Al_2O_3 \cdot 3H_2O$) begins to precipitate. Upon stopping the mixer, the solids quickly settle to the bottom of the reactor, much like sand. Figure 1 shows the thermodynamic relationship between the stability fields for soluble aluminate (AlO_2^-) and insoluble gibbsite and the aluminum cation as a function of pH.

As shown in Fig. 1, as aluminum metal is added to the alkaline solution in the pH range of 12—14, the soluble aluminate anion predominates until, after a sufficiently large quantity of aluminum has been added and reacted, we reach the gibbsite/aluminate equilibrium line separating the soluble aluminate and the gibbsite stability fields. After the solution reaches this point, any further addition of aluminum metal causes the formation of the highly insoluble gibbsite product.

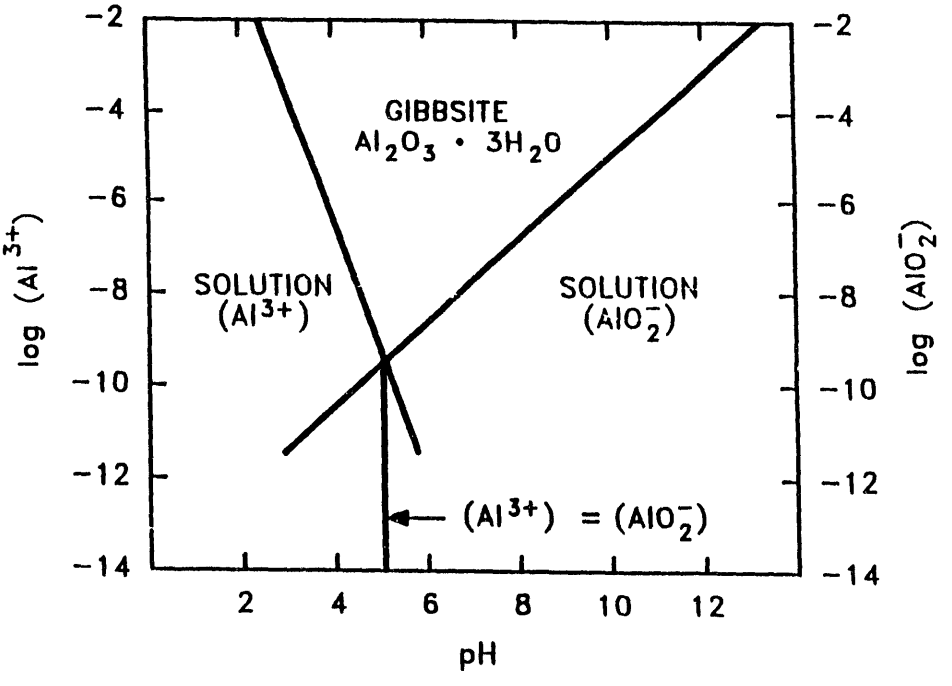

Fig. 1. Stability field diagram for the aluminate-gibbsite system.

In the NAC process, aluminum dissolves, functioning similarly to a sacrificial anode, and therefore we can write the following equation for the sodium nitrate reduction reaction if the process is assumed to be 100% efficient:

$$6NaNO_3 + 16Al + 24H_2O \rightarrow 6NH_3 \uparrow + 5Al_2O_3 \cdot 3H_2O + 6NaAlO_2 \qquad (4)$$

This reaction shows that we can expect to use 0.8 kg of metal per kilogram of sodium nitrate to reduce all the nitrate. Preliminary test work performed in the past showed that half of the metal was consumed while reducing the last 10% of the nitrate in solution due to the much lower nitrate concentration relative to the amount of water near the end of the reaction; this finding forced us to use twice the amount of aluminum shown in reaction 4. This was predominantly the case when operating in the batch mode; however, the use of a continuous recycle mode in which solids are constantly removed from the reactor has increased the efficiency to the point that we now require only 10% above theoretical.

Because our prior batch reaction tests showed that we must use almost twice as much metal as predicted by reaction 4 to convert all of the nitrate, we can write a reaction that reflects a situation in which we might run that batch reactor until nearly all the nitrate is converted to ammonia. This equation would apply when the concentration of nitrate drops too low in the batch mode and also, to a limited extent, in the continuous mode.

$$6NaNO_3 + 32Al + 72H_2O \rightarrow 6NH_3 \uparrow + 24H_2 \uparrow + 13Al_2O_3 \cdot 3H_2O + 6NaAlO_2 \qquad (5)$$

Based upon this reaction we would expect to use 1.6 kg of metal per kilogram of sodium nitrate. Our process, like others, can be performed continuously in a way that does not, until the end, allow the nitrate concentration to drop into a low range in which hydrogen can be produced; therefore, we are able to avoid hydrogen production as predicted by equation 5.

As both reactions 4 and 5 show, a large amount of water is consumed, much of which supplies aluminum with its oxygen component and ammonia with its hydrogen. This means that nearly all of the water contained in a 4 M nitrate solution is consumed during the reaction, and water must be added during the reaction to facilitate mixing and enhance heat transfer to the cooling system. This is especially true when operating in the batch mode, where the percentage of solids in the reactor may climb very high and impede mixing and heat transfer.

Reactor Products and the Addition of Silica

The primary product from the reaction of aluminum with a basic solution of sodium nitrate is gibbsite (94-96%), with a small amount (3-4%) of sodium aluminate and only a trace amount of caustic. Because of the ability of aluminate to hydrolyze and form more solid gibbsite, the analysis is a difficult one. For this reason, the ratios of gibbsite to aluminate in the final product based upon reactions 4 or 5 do not agree, because we evaporated the final product slurry. This analysis is based upon evaporating the contents of a batch reactor to determine the ratio of these species by both X-ray and wet chemical methods, which agreed well.

In addition to aluminum that is added to the reactor, 40 μm silica (quartz form) is also added for the purpose of reacting with sodium during the sintering stage of the reactor products. Ideally we added one mole of silica per mole of sodium contained in the waste solution in order to form the mineral nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) in the final ceramic product; in this way even sodium will be bound in the ceramic

product. We are presently experimenting with various ratios above and below the ideal 1:1.

The product exiting the reactor is sandlike and easily dewatered. If allowed to stand in the reactor for a number of hours, it will "age" and become hard; afterwards it cannot be dissolved in acid. After this type of aging, in which three-dimensional bonding between aluminum and oxygen and some hydrogen occurs, the product can be dissolved only in boiling sodium hydroxide solutions and then only with difficulty.

The reactor product is dried and then calcined at between 600 and 800°C. This product is then uniaxially pressed at 69 MPa (10,000 psi) and sintered in the range of 1300 to 1400°C as is done with other ceramics. A simple schematic flow sheet of the process involving these steps is presented in Fig. 2.

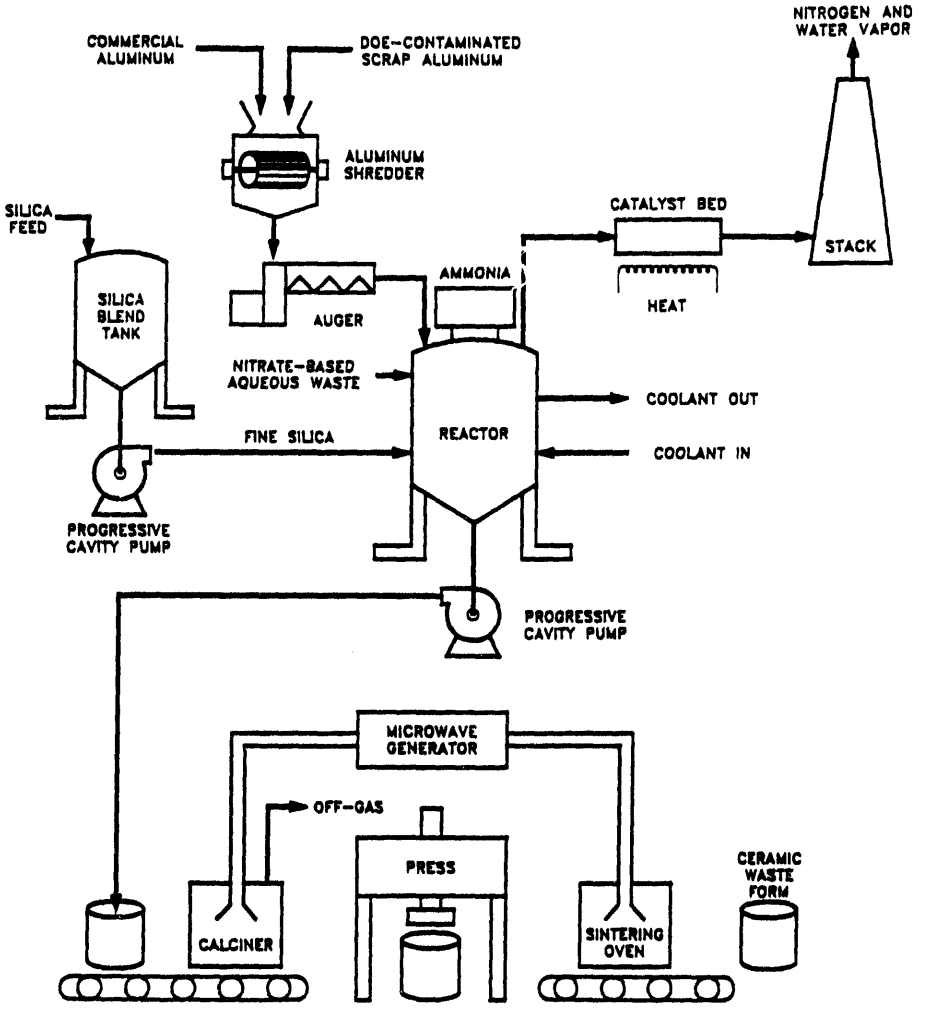

Fig. 2. General flow sheet for the NAC process.

Sintering of the product causes fusion to occur between alumina particles where contact is made between them, thereby increasing the physical strength. A product containing nepheline and mullite fused to alumina particles is formed with a final density of ~2.8 g/cm^3 at present.

Additionally, the size of the gibbsite particles forming *in situ* in our reactor is known to be primarily submicron, based upon the literature and upon our observing material pass through filter paper in the laboratory. Because of these small dense particles, we have an opportunity to produce a solid with much smaller pores than any cement-based material. Therefore, the capillary pore pressure resistance inside such a solid will be very high as is the case with most ceramics. Water from the outside will not be able to penetrate, as it can with cement-based grout or even with high-grade structural concrete. Small pores and therefore capillary resistance also inhibit the ability of ions to diffuse into or out of such a ceramic product without this necessary water.

Potential for Large Volume Reductions

If a nitrate-based waste is immobilized in a cement-based grout, as is done at Savannah River or at Oak Ridge's Melton Valley, we can expect a volume increase of between 35 and 50%, depending upon the formulation used. In Oak Ridge's Melton Valley, we are grouting 4 M sodium nitrate and obtaining a 40% increase in volume. Figure 3 shows this relative volume change between cement-based grout and the NAC process.

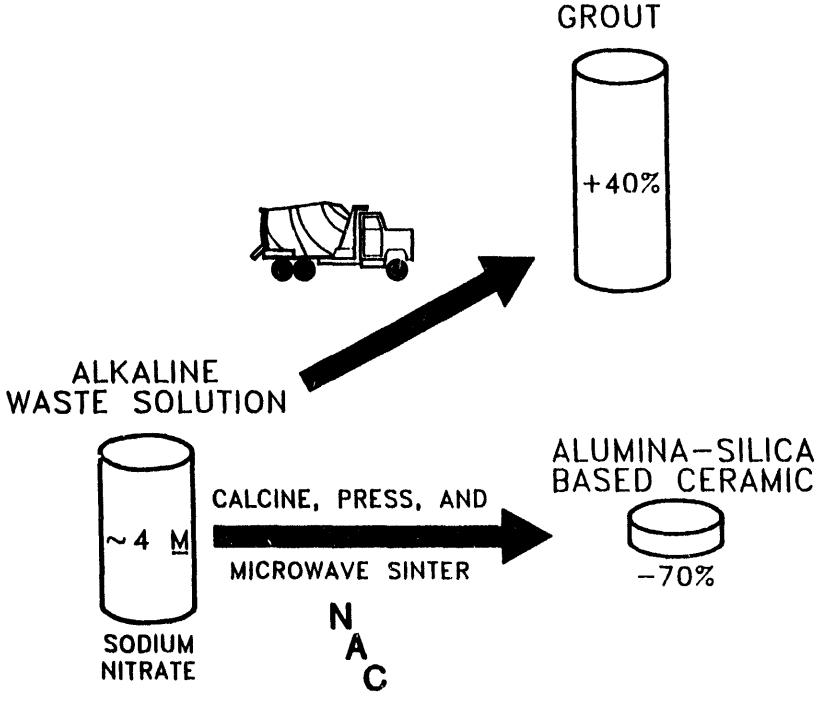

Fig. 3. Relative volume reduction efficiencies of the NAC process compared with cement-based grout.

The Fate of Other Waste Solution Cations

This process has an added bonus aside from converting nitrate to ammonia; that is, it also precipitates most cations, metallic and nonmetallic, from solution and forms "highly" insoluble aluminates. Because aluminate is an important intermediate species in our reaction, this anion is always present and forms what are referred to as "spinels" in the field of material science. These spinels of monovalent and divalent cations can be represented as $R_2O \cdot 11\ Al_2O_3$ and $RO \cdot 6\ Al_2O_3$ respectively. In fact, the spinel calcium aluminate is the active ingredient in Portland Cement (~10%) and is known to be quite insoluble. As a result, we would expect that the sister alkaline earth species, such as strontium, will form a spinel with properties similar to those of calcium. The higher the positive charge to ion radius ratio of the cation, the more insoluble is the resulting spinel (1, 2).

This fortuitous chemical property of the aluminate anion means that most metal and nonmetal cations will enter the dense solid ceramic matrix as a very insoluble mineral. Additionally, some chemical species in the waste solution may be adsorbed onto the large specific surface area of the reactor product; this may also include some organics which could be removed during calcining.

Ammonia Disposal

It is obvious that we will produce large amounts of ammonia upon reducing nitrate. In our laboratory tests we scrub the ammonia into dilute acid. This scrubbing option is only one of several that can be utilized for ammonia disposal. The following are a few possibilities which are "off-the-shelf" technologies:

- The ammonia can be scrubbed into dilute acid to form ammonium salts.
- The gas can be cooled and pressurized into liquid ammonia for reuse.
- The ammonia can be burned in a heated catalytic bed tower to nitrogen and water vapor (3). This is likely the preferred disposal scenario.
- The ammonia can be reoxidized to form nitric acid for reuse on site.

Drying or Sintering Reactor Products

The discharged product from the reactor is very amenable to microwave drying, calcining, and sintering because it is primarily alumina and silica. If dewatered, dried, calcined, and compacted uniaxially in a container prior to sintering, a hard ceramic may be produced through the use of microwaves in the 28-GHz range.

What is also fortuitous about the use of microwave processing is that alumina is well suited to this technique because it is transparent to microwaves. It has a large "skin depth" (penetration depth), as much as 3 to 6m compared with only a few centimeters in a sodium nitrate–based solution. Use of microwaves means uniform heating and the potential to sinter at much lower temperatures (4) than those possible with conventional convective heating systems.

ADVANTAGES OF THE NAC PROCESS OVER OTHER PROCESSES

Because nitrate is such a very mobile anion, it is difficult to immobilize it in materials such as polyethylene and bitumen, which are subject to osmotic pressure swelling over time and can burn on their own, once ignited with difficulty, because nitrate carries its own oxygen. Additionally, no cement-based formulation is known that can prevent the diffusion of nitrate or nitrite out into the environment when water is present.

Because of the ease with which nitrate is leached from grout, we place the grout inside concrete vaults to slow release. The pore water inside the vault walls will eventually equilibrate with the nitrate ion

concentration in the grout pore water and then the release to the environment begins. In this case the vault is another barrier that will eventually release nitrate as well, but at a reduced rate. The vault is also subject to degradation by the elements and the forces of nature with time.

In the case of cement-based grout, we pay a large price for the volume increase that results when we place an aqueous waste in such a matrix. We can expect large volume increases, as shown in Fig. 3, when using such a matrix.

Instead of immobilizing nitrate in a porous, solid matrix such as grout, the option of converting it to another form such as a gas exists, thereby obviating the problem of nitrate release. However, such processes may be hindered by problems associated with off-gas processing (e.g., NO_x scrubbing). Four possible options for treating nitrate are (1) thermal conversion to NO_x, (2) electroreduction to N_2 and NH_3, (3) biodenitrification to N_2, and (4) organic reduction to NO_x at a low pH.

Thermal Conversion

Although the reported values for the initial temperature of thermal decomposition of sodium nitrate vary widely, depending upon the reference source, decomposition starts at about 588°C and is 70% complete at about 940°C. This conversion to NO_x and sodium oxide can occur only after all water has been evaporated, a very energy-intensive process step. Different types of such decomposition are reported throughout the literature (5, 6).

A problem for such technology is that the scrubbing of NO_x is still partly science and some art. The lower oxides of nitrogen such as NO(g), which have a low aqueous solubility, are often not removed and need to be reoxidized and rescrubbed in many stages, only to produce another nitrate/nitrite-contaminated waste stream, possibly containing radioelements. Additionally, radioelements that become volatile in the temperature range of 588 to 1200°C must be scrubbed out, thereby producing yet another separate waste stream.

In addition to problems with NO_x and radioelement scrubbing, organics present in the nitrate-based waste may initiate an explosion depending upon concentration, and other catalyzing metals or species which may be present in the waste.

Electroreduction

A number of different electrolytic cell configurations exist and, depending upon the cell, can produce a mixture of gases such as NH_3, N_2, O_2 and H_2 (7-10). Such cells are subject to a number of problems:

- All of these cells produce 40 kg of sodium hydroxide for every 85 kg of sodium nitrate processed. The NAC process produces aluminum oxide and sodium aluminate instead of caustic and brings with it the benefits associated with these components as discussed above.
- In-cell crystallization of salts, due to evaporating liquid, foul electrodes and lower current efficiency. Criticality issues may become a concern with Hanford wastes.
- Trace amounts of chromium (<36 ppm) can drop cell efficiency from the high nineties down to the thirties due to cyclic oxidation and reduction of chromium in such cells; the result is that decomposition times may quadruple. The NAC process is unaffected by chromium because this species can form a highly insoluble aluminate as discussed in the literature.
- Many metals and some radioelements plate out on electrode surfaces and lower cell efficiency.
- The electrolytic process does not bring with it the potential for producing its own waste form, as does the NAC process, and the associated chemistry that makes alumina-silica such a good host matrix.

Biodenitrification

The biodenitrification process produces nitrogen and copious amounts of carbonate when run anaerobically (11-15), which happens to be the most efficient mode. The bacteria must be fed a carbon source such as an acetate, which is oxidized to carbon dioxide while reducing nitrate. Also, a phosphate-containing salt for intercellular energy transfer and storage must be added. This produces large volumes of carbonate salts which must be disposed of.

The biggest problem with the use of bacteria is that they must operate in the proper pH range (7 to 8.5) and therefore will require pH adjustments downward for Hanford waste. Additionally, certain concentrations of various metals can be toxic to bacteria cultures. Further, the total salt concentration cannot be too high, because the bacteria will lice due to osmotic pressure imbalance, and consequently, initial dilution of the Hanford waste may also be required.

Organic Reduction in Acid

This technology is very old and was developed in Europe by the Germans (13, 16, 17). In this process the nitrate-containing solution "must" be acidic before it can be utilized, and therefore vast amounts of acid would likely have to be added to the Hanford waste, depending upon waste-buffering capacity. In this process, acidic, nitrate-based solutions are heated, and an organic compound such as sucrose, formaldehyde, or formic acid is slowly added to produce NO_x and carbon dioxide as well as a lot of heat.

The process is difficult to control and is sometimes explosive. In addition, any acid chosen to lower the pH of the Hanford solution will create problems. Corrosion problems will follow the use of hydrochloric acid. Sulfuric acid will produce large amounts of the high-volume hydrated calcium sulfate (gypsum). Nitric acid may be the only remaining choice, even though it creates more nitrate, which must be removed later. Because nitric acid, like hydrochloric acid, provides only one proton, vast amounts of acid (and consequently nitrate) would be necessary if these acids were utilized.

CONCLUSIONS

The experimental results obtained to date confirm that the NAC process will reduce the nitrate present in Hanford aqueous, sodium nitrate–based waste to ammonia and hydrated alumina. When used in combination with silica, reactor product can be used to produce an alumina-silica-based ceramic. The reaction is exothermic and requires cooling to control the reactor temperature to between 50 and 60°C. Upon using a motorized auger to feed aluminum powder to an ethylene glycol–cooled reactor, we have shown that the reaction can be easily controlled at temperatures between 50 and 60°C.

Utilizing Hanford supernate at concentrations of between 6.2 and 3.1 M sodium nitrate, 90–99% of the nitrate present can be converted to ammonia, the converted percentage being primarily dependent upon the ability of the mixing system in the reactor to stir the solid/liquid slurry when the batch mode is used. If the process is run in the continuous mode, high concentrations of nitrate can be treated at still higher overall efficiencies.

Bench-top experiments showed that aluminum can be pumped to the reactor as a slurry of aluminum powder and water, in addition to using a motorized auger. The water-slurry feed has the advantage of adding needed water to the reactor to replace the water taken up as the aluminum reacts to form crystalline gibbsite.

Addition of the aluminum to the reactor in the form of larger particles reduced problems encountered with the fine dry powder feed by preventing caking from water vapor condensation. The larger particles of aluminum also reacted more slowly than the fine powders and required less cooling and temperature control.

Reaction rates for the various experiments were calculated to give a rough idea of what might be expected for a pilot-plant design. The rates were based upon a differential nitrate reduction at a point in the reaction

where nitrate was being actively reduced, usually when at a point between 70 and 150% of the theoretical amount of aluminum had been added. These rates were between 80 and 300 g $NaNO_3$/liter of starting reactor volume per hour. Based upon these numbers, a preliminary estimate was made for a full-size plant to treat the Hanford SST waste at 1200 kg NO_3/h over a 20-year period. The engineering cost estimate and its assumptions are presented in the appendix of our draft report on work performed last year; the report is available upon request (18).

The cost estimate for a full-scale nitrate processing plant assumes a batch reactor with unit costs of \$2.01–\$2.66/kg of nitrate to process the Hanford nitrate waste over 20 years. The cost of aluminum is a major part of the overall cost, making reaction efficiency even more important. The operating cost compares with published literature costs for the electrolytic process and thermal processing in 1957 of \$5.13/kg of nitrate.

Results of this study have shown that the product exiting the reactor can be uniaxially pressed as any other ceramic to result in a 70% volume reduction based upon the starting volume of the original waste solution. All the water associated with the waste solution is consumed by the aluminum to form oxide.

The effective treatment of the Hanford nitrate-based wastes is dependent upon the development of simple and effective technologies such as described in this work. Continued work in FY 1993 will focus upon the waste form properties such as leaching resistance for sodium and many other species of interest to Hanford.

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BENCH-SCALE VITRIFICATION OF LOW LEVEL RADIOACTIVE WASTE

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ABSTRACT. The vitrification treatability study described in this paper was carried out following U. S. Environmental Protection Agency (EPA) guidance for Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites. A tiered experimental approach was used which consisted of remedy screening and remedy selection tiers. This paper examines the vitrification of eight waste streams and reports results from the remedy screening tier. The performance of various vitrified products was determined on composite waste samples. Local soil, local fly ash, and sodium salts were used as glass formers and fluxes. Multiple additive loadings were investigated for each waste stream. The leachability of the product was characterized by volume modified Toxicity Characteristic Leaching Procedure (MTCLP) and modified Product Consistency Test (MPCT) procedures. Successful formulations were determined for all wastestreams.

INTRODUCTION

IT was contracted to evaluate remedial technologies at a client's site. This site's material contains Resource Conservation Recovery Act (RCRA) metals, anions, such as, fluoride, sulfate, and nitrate, and radionuclides, e.g., uranium. The physical consistency of the material varies from mineral material to sludge. The technologies to be considered were to lower the leaching of contaminants from the material by chemically fixing them in an altered matrix or by reducing their concentration in the original matrix. The remedial technologies investigated were cement-based stabilization, vitrification (ex situ), and selective chemical extraction techniques.

Treatability Study

The treatability study design followed the U.S. Environmental Protection Agency (EPA) "Guide for Conducting Treatability Studies Under CERCLA" guidance.(1) The remedy evaluation phase may require three (3) tiers of the treatability testing:

- Remedy screening
- Remedy selection
- Remedy design

The IT treatability laboratory was contracted to complete the first two tiers.

As described in the EPA guidance, remedy screening is the first step in the tiered approach. Its purpose is to determine the feasibility of the treatment alternative. Typically these tests are conducted under conditions favorable to the technology. These small-scale studies are designed to provide a qualitative evaluation of the technology and are conducted with minimal levels of Quality Assurance/Quality Control

(QA/QC). Tests conducted under this tier are generic in nature (not vendor specific). If the feasibility of the treatment cannot be demonstrated, the alternative generally should be eliminated.

The remedy selection tier is designed to determine whether a treatment alternative can meet the cleanup goals and at what cost. The purpose of this tier is to generate the performance data and data for the estimation of the cost at a +50/-30 percent accuracy. Remedy selection studies are typically small scale, incorporating generic tests using bench- or pilot-scale equipment in either the laboratory or the field. The levels of QA/QC are moderate to high.

This paper will cover only the remedy screening tier vitrification results. The vitrification technology was investigated on multiple waste streams. Eight different waste streams will be covered in this paper. Compositional analyses provided the quantity of glass formers and fluxes in the waste streams and reagents to be used in the range finding experiments to determine potentially promising formulas. The best formulations from the range finding study were used to make five formulations per waste stream for the leaching tests. (Specific modifications carried out in the leaching tests is discussed below in Sections 2.6.1 and 2.6.2.) Figure 1 shows the process discussed in this report.

Vitrification Technology

Vitrification of hazardous or radioactive material is a process where the material is converted into a glass or glass-like substance through a thermal process.(2-12) The process has flexibility to treat a wide variety of inorganic and organic species. The inorganic species are incorporated into the glass matrix while the organic species are destroyed by pyrolysis or combustion. In addition, the volume of the treated waste is often substantially less than the original waste volume.

Vitrification is the only accepted treatment of high-level radioactive waste (HLW) in the United States.[1] Vitrification is being considered for treatment of low-level radioactive waste because of the potential to lower the cost of disposal and to lower emissions from the treated product. Also, the EPA has selected vitrification as Best Demonstrated Available Technology (BDAT) for arsenic.(13)

Vitrified products exhibit substantial chemical and physical durability. Chemical durability is the ability of the product to withstand attack by leachants in the environment or in the laboratory. Physical durability is the resistance of the product to degrade as a result of mechanical and environmental stress.

The high chemical durability (leach resistance) is due to the chemical bonds and effective encapsulation of contaminants within the glass matrix formed during the melt or after the melt solidifies. In the vitrification process, the inorganic contaminants are melted or dissolved into the molten liquid (solvent). The process disperses the contaminants to form a homogeneous liquid. If the molten liquid is cooled quickly enough and the melt composition is in the correct range, a homogeneous glass without crystals will form. The contaminants in the glass product will be either chemically incorporated or encapsulated into the glass matrix. Both covalent and ionic bonding mechanisms will function to incorporate the contaminants. Some materials, e.g., platinum, do not bond well with the silicate glasses. These materials will be encapsulated by the vitrified product. Encapsulation inhibits the leaching of these materials from the glass product.[14,1]

In the field, there are two different vitrification approaches, i.e., in situ (ISV) or ex situ. The ISV process is conducted without prior removal of the contaminated material from its current location. Typical operating temperatures range from 1600° to 2000°C.(6-12) In the ex situ process, the waste is removed from its current location and treated in a melter or furnace. Additives are mixed with the waste to produce the desired physical characteristics of the melt and the vitrified product. The ex situ process has an advantage over ISV because there is greater control of the feed and reactor. Typical ex situ operating temperatures range from 1000° to 1600°C.(1,15) Only the ex situ process was considered for the treatment of the client's waste.

EXPERIMENTAL

Compositional Analyses Of Waste And Additives

The major glass components of the waste, local soil, and local fly ash were determined to assist in the formulation development of the various waste streams. In the analysis, all of the metals were assumed to be oxides in their normal highest oxidation state. The compositional analyses did not take into account the presence of anions such as fluoride and sulfate. The dry blend formulations of waste and additives were selected for the initial range finding experiments based on the compositional analyses. Each dry blend formulation was selected such that enough local soil or fly ash was added to the waste streams to form a melt with 30 to 60% glass formers. The other initial range finding experiment was to melt the waste with no additives mixed with the waste. These range finding experiments were conducted in alumino-silicate (firebrick) crucibles. Additional soil or fly ash was added to the next range finding experiment if the solidified product did not look like a glass, or had obvious crystal in it, or if the melt was very fluid or the melt rapidly dissolved the alumino-silicate crucible. If the mixture did not melt at 1250°C or if the melt was very viscous, more sodium salt (sodium hydroxide or carbonate) was added to the waste. Table 1 presents the results of these analyses. The table separates the results for glass formers and fluxes.

Additives

The reagents used were local soil, local fly ash, sodium hydroxide, and sodium carbonate. The soil and fly ash were added to provide glass formers while the sodium compounds were used to lower the melting point of the melt and to decrease the viscosity of the melt. If the viscosity of the melt was too high, the contaminants would not be evenly dispersed in the melt, the melt could not be poured from the crucible, and at times bubbles would form in the solidified product.

Feed And Reagent Preparation

The waste streams and additives were dried at 105°C to remove the excess water before grinding to a powder. The dried material was placed in firebrick crucibles. If sodium hydroxide was to be added to the mixture, a solution of the hydroxide was well mixed with the dried waste. The waste and additives were calcined at typically 200°, 400°, and 750°C to drive off volatile organic compounds, oxidize remaining organic compounds, and drive off carbonates, nitrate, and water while transforming the waste and additives to oxides. This calcination process simulates the chemical decompositions that may occur in the cold cap of an ex situ melter. The 200° and 400°C calcination steps were for about 2 hours each. The 750°C calcination step was normally overnight (8 - 12 hours) to oxidize the high organic content in the local fly ash and in several of the waste streams. It was critical to destroy the organic compounds in the feed in order to ensure that the melt was not under reducing conditions. If metals are reduced in the melt, they may form a lower melting point alloy with the platinum/gold crucible that would destroy the crucible. Also, reduced metals pool at the bottom of the crucible forming a non-homogeneous product. This latter situation may lower the chemical and physical durability of the vitrified product.

The calcined wastes and additives (local soil or fly ash) were mixed together in the assigned proportions, then ground again to ensure good mixing of the waste and additives. This mix was added to the crucibles.

Crucibles

Three types of crucibles were used during the remedy screening studies. These consisted of alumino-silicate firebrick, platinum/gold, or stainless steel crucibles. The platinum/gold crucibles were used after the initial range finding experiments. Crucibles made from platinum/gold (five percent gold) were used for samples

planned for leaching tests. These crucibles are non-wetting to silicate glasses allowing all of the solidified product to be removed from the crucible. The complete sample could then be used for further testing. With the firebrick crucibles, significant intrusions of glass formers from the crucibles into the melts were observed. The intrusion of silicon and aluminum into the melt would produce a more durable glass product and a higher viscosity melt than the equivalent waste/additive formulation would have without the intrusion. The stainless steel crucibles were used after the degradation of the platinum/gold crucibles was observed in the presence of local fly ash.

Performing Melts

The following is the procedure used for experiments where the leachability of vitrified product was to be evaluated. The melts were performed on the calcined feeds in a preheated Lindberg Model 51333 box furnace at 1250°C for 4 hours. The melts were stirred with a platinum wire after 2 to 3 hours in the oven. Mixing the viscous liquid was critical to ensure that a homogeneous product was produced. After 4 hours in the furnace, the molten samples were removed from the ovens and allowed to cool rapidly. In order to minimize the potential for crystal growth in the product, the temperature of the melt was ramped down from 1250°C to about 600°C in 20 minutes while the crucibles remained in the furnace.

The glass product was ground in a Tekmar mill or a Brinkman centrifuge grinder for size reduction necessary for the MPCT and MTCLP leaching tests. The leaching tests are described in section 2.6. The 100 to 200 mesh size (75-150 microns) sample was collected for the MPCT test, while the smaller size fraction (less than 75 microns) sample was used for the MTCLP.

Leaching Tests

Information from compositional analyses and range finding experiments was used to derive formulas for samples. These samples were used in the leach tests. The leach tests consist of the MTCLP and MPCT analyses. Table 2 presents the design of the formulations used in the leaching tests. Five formulations were used, four containing soil or flyash addition, while the "as-is" formulation only had Na_2O addition. Two different loadings of Na_2O were investigated. Table 3 shows the range of reagent additions for each of the samples.

Modified Toxicity Characterization Leaching Procedure (MTCLP). In the TCLP (16), the material to be leached is ground to less than 3/8 inch, leached in an acetic acid solution at room temperature for 18 hours. The liquid to solid ratio is 20 to 1.

The MTCLP is a modification of the TCLP test. The same leachate to solid ratio and leachants (TCLP Type 1 and 2) are used in both procedures. The MTCLP differs from the standard TCLP as follows: the MTCLP uses 2.5 to 10 grams of material instead of 100 grams; the MTCLP generates 50 to 200 milliliters of leachate instead of 2 liters; and the leachate is analyzed for metals rather than metals and organics. For the remedy screening tier of this project, the glass product was ground to less than 75 microns instead of less than 3/8 inch in the TCLP test. By grinding all of the glass product to a powder, the surface area to weight ratio of the glass is increased. This was done to make the MTCLP test more aggressive and to highlight the less chemically durable glass products.

The MTCLP leachate was analyzed for selected RCRA metals, pH, and target radionuclides. The selected RCRA metals analyzed were arsenic, barium, cadmium, chromium, lead, selenium, and silver. The target analyses for radioactivity were uranium concentration, and gross alpha and gross beta.

Modified Product Consistency Test (MPCT). The PCT evolved from the MCC-3 test and was developed for evaluating high-level vitrified waste forms from the Defense Waste Processing Facility at the Savannah

River Site.[1] The glass product is ground to 74 - 149 micron size, rinsed with water and absolute ethyl alcohol, and leached in deionized water at 90°C for seven days. The volume of leachate to weight of glass ratio for the PCT is 10 mL/g. In the PCT, each glass sample is set-up in triplicate to determine the precision of the test. The MPCT differs from the PCT in that only one sample was leached instead of triplicates and the leaching vessels were polyproplyene bottles instead of stainless steel or Teflon™ vessels. Tests were conducted initially in triplicate on a standard mixed waste vitrified product to determine if using a plastic leaching vessel would significantly affect the result. The leachate concentrations in the IT experiments using plastic leaching vessels were within the range of values measured by other contractors using the standard PCT procedure.

The MPCT leachate was analyzed for selected metals, radionuclides, pH, and anions. The selected metals and radionuclides analyzed were aluminum, boron, calcium, iron, potassium, lithium, magnesium, sodium, silicon, and uranium. Chloride, nitrate, and sulfate were the anions analyzed for in the MPCT.

The leachate concentrations were analyzed by two methods. The first method is the absolute concentrations of the target compounds in the leachate. This method will not be discussed in this paper. The second method is the normalized leach rate (NLR). This latter leaching rate normalizes the leaching rate to the amount of element *i* in the glass per day per meter squared of surface area of glass. The NLR for component *i* is calculated as follows:

$$NLR_i = \frac{Conc_i(mg/L)}{S/V(m^{-1}) * time(d) * f_i}$$

where
NLR_i = NLR for component *i*,
$Conc_i$ = Concentration of elemental component *i* in the glass product,
S/V = Surface to volume ratio (set at 2000 m^{-1} for the PCT)
time = Duration of leach test,
f_i = The fraction of element *i* in the glass.

The NLR values for the glass products will be compared to Savannah River Site high level waste (HLW) NLR criteria of 1.0 $g/m^2 \cdot d$.

The PCT procedure calls for 90°C leaching temperature. This temperature was based on the self-heating of the HLW. Since the waste streams in this project were low-level radioactive waste, there will be no self heating of the glass as is observed with HLW. Therefore, based upon reported kinetic data, the measured NLR_i for the vitrified products should be at least one to two orders of magnitude greater than the actual leach rate that would exist at ambient temperature in a storage cell.(1,7)

Analytical

The RCRA metals and uranium in the compositional and leaching tests were analyzed on a Thermal Jarrell Ash ATOMSCAN 25 inductively coupled plasma emission spectrometer (ICP) using SW-846 method 6010. The samples were digested by SW-846 method 3051 (microwave digestion) (17).

Uranium was also analyzed by an IT procedure that couples ion chromatography (IC) equipped with a post column reactor to a fluorescence or phosphorescence detector. This procedure gives rapid results and lower detection limits than the ICP analysis for uranium. A typical equipment list for this analysis is Dionex liquid chromatographic module, Dionex post-column reagent delivery module, CS 5 analytical column, CG 5 guard column, LCD Milton Roy Constametric III HPLC pump, and Perkin Elmer LS30 luminescence detector.

The gross alpha and beta were determined on a Canberra Model 2404F counting system with proportional gas flow detector. The counting times were from 5 to 30 minutes depending on the activity and the matrix of the sample. Solid samples were typically counted for 30 minutes.

RESULTS AND DISCUSSION

Range finding tests were done initially to determine the minimum soil and fly ash additions necessary to produce a glass-like product as judged visually. Results of waste, soil and fly ash compositiona! analyses (Table 1) were used to design the composition of waste/additive mixtures in these range finding tests. Initial glass formulations were based on the sodium silicate model with the objectives of greater than 35 percent glass former content with a former to flux ratio of at least 0.5 in the melt. Formulations were further guided by an attempt to maximize waste loading and minimize the sodium/flux addition while maintaining a viscosity of 20 - 100 poise at temperature of 1250°C. In the leaching study, each waste/soil and waste/fly ash mixture chosen was then processed at two different sodium/flux levels to vary viscosity and provide observations on glass processability. See Table 2 for the general formulation matrix used in the leaching study. In seven of the eight waste streams the ability of each waste stream to vitrify was tested without soil or flyash addition in addition to formulas containing soil and fly ash additions. The melt viscosity of waste stream A, with a glass formulation/flux ratio of 0.073, was unacceptably low for this project. When the waste was heated in firebrick crucibles, the melt rapidly dissolved the crucible. Table 3 presents the vitrification formulas for each waste stream derived from the range finding tests.

An initial complication to this testing program was the detrimental interaction of some waste streams with the platinum/gold crucibles. Incompletely combusted carbon and base metals in the fly ash produced reductive melts during vitrification processing. This resulted in the formation of platinum/base metal (e.g., iron) alloys with melting points well below the process temperature of 1100° - 1250°C and the consequential destruction of the crucibles. Testing was continued using firebrick crucibles which allowed the study to continue but introduced the problem of crucible components (e.g., aluminum and silicon) being incorporated in the glass melts. The greater concentration of glass formers in the melt increased the viscosity making the molten glass non-pourable. Also, the firebrick crucibles did not free-release the glasses, therefore, the sodium salt flux additions were increased as necessary to achieve the desired 20 - 100 poise viscosity range and allow the molten glasses to be poured into graphite crucibles to allow free-release of the glass after cooling.

Processing the 41 formulations specified in Table 3 led to a number of interesting observations regarding differences among formulations as well as differences within waste streams between waste/soil and waste/fly ash mixtures. Waste streams without additives produced vitrified products ranging in character from black friable granules (stream E), to granite-like with glassy intrusions (stream D), to single phaseceramic (stream F), to mixtures of ceramic, glassy and granite-like phases (streams A,B,C), to brown or black obsidian (streams G,H).

Table 1. Composition of Waste Streams and Vitrification Additives

Waste Stream	Glass Formers (mole %)	Fluxes (mole %)	Former/Flux Ratio
A	0.83% Al_2O_3 0.26% Fe_2O_3 5.67% SiO_2 6.76%	7.08% CaO 85.84% MgO 0.32% Na_2O 93.24%	0.073
B	6.0 % Al_2O_3 1.82% Fe_2O_3 57.85% SiO_2 65.67%	18.48% CaO 14.53% MgO 1.32% Na_2O 34.33%	1.913
C	7.02% Al_2O_3 2.74% Fe_2O_3 38.46% SiO_2 48.22%	23.12% CaO 27.01% MgO 1.65% Na_2O 51.78%	0.931
D	1.85% Al_2O_3 0.65% Fe_2O_3 15.79% SiO_2 18.29% (4.63% UO_3)	10.29% CaO 66.20% MgO 0.58% Na_2O 77.07%	0.237
E	1.82% Al_2O_3 2.38% Fe_2O_3 8.74% SiO_2 12.94%	53.40% CaO 27.08% MgO 6.58% Na_2O 87.06%	0.149
F	4.30% Al_2O_3 1.12% Fe_2O_3 19.21% SiO_2 24.63% (1.30% UO_3)	26.98% CaO 46.86% MgO 0.23% Na_2O 74.07%	0.333
G	8.36% Al_2O_3 2.92% Fe_2O_3 59.3 % SiO_2 70.58%	19.14% CaO 8.38% MgO 1.89% Na_2O 29.41%	2.40
H	3.83% Al_2O_3 1.96% Fe_2O_3 32.7 % SiO_2 38.49%	59.82% CaO 0.95% MgO 0.74% Na_2O 61.51%	0.626
Soil	4.25% Al_2O_3 1.27% Fe_2O_3 58.68% SiO_2 64.20%	24.95% CaO 9.44% MgO 1.41% Na_2O 35.80%	1.79
Fly Ash	23.13% Al_2O_3 4.31% Fe_2O_3 67.54% SiO_2 94.98%	2.57% CaO 1.93% MgO 0.52% Na_2O 5.02%	18.94

Notes: Based on dry weight basis (105°C). Does not account for anions e.g: Cl^-, F^-, SO_4^{--}, and NO_3^-.

Waste stream/soil mixtures produced in all cases a glass-like product although the homogeneity varied significantly. Very good single phase brown to black glasses were observed (streams F,G,H) but in some cases the glasses were opaque (streams A,B,C,D). In one case (stream E), the mass of material in the crucible formed a black glass but a separate phase of yellow glass was observed on the surface and at the crucible interfaces. This "bumblebee" glass with separate solid phases may be caused by the concentration of sulfate being higher than could be incorporated into a single phase glass.

Table 2. Formulation Matrix For Leach Test

Run No.	Waste	Soil	Fly Ash	Na_2O
1	X	—	—	X
2	X	X	—	Lo
3	X	X	—	Hi
4	X	—	X	Lo
5	X	—	X	Hi

X=present
—=absent

Table 3. Vitrification Formulations

Waste Stream	Waste (g)	Soil (g)	Fly Ash (g)	Na_2O (g)
A	100	0-150	0-200	2.5-5.2
B	100	0-50	0-100	2.5-10
C	100	0-50	0-100	2.5-7.5
D	100	0-150	0-200	0-7.5
E	100	0-250	0-250	8-20
F	100	0-150	0-200	2.5-8.5
G	100	0-50	0-100	8.2-11.9
H	100	0-50	0-100	2.5-12.5

For waste streams supplemented with fly ash, sodium/flux loading had a pronounced impact on the homogeneity of the glass and the degree of intrusion of the crucible material into the vitrified product. While four of the waste streams (B,C,G,H) produced very good glasses across sodium loadings, others exhibited variable homogeneity with sodium/flux loading (stream E), striated ceramic-like intrusions (stream D) or modified glass at the crucible interface where corrosivity or low viscosity dissolved the firebrick crucibles (streams A,F) and contributed to the vitrifying waste matrix.

The leachability of the vitrified waste stream products was evaluated by modified versions of EPA's TCLP (MTCLP) and Savannah River Site's PCT (MPCT) leach tests. It should be noted that while the MTCLP procedure scaled down the volume of material tested, it utilized a less than 75 μm size fraction for leaching instead of the EPA specified less than 9.5 millimeters. Thus with a significantly increased surface area exposed to leaching, the MTCLP represented a more aggressive leach test than the TCLP. The MPCT in its reduced scale modification from the full scale PCT utilized the specified 75 - 150 μm glass particle size fraction.

Across the eight waste streams investigated, all 41 formulations passed the EPA's TC regulatory limits for the target RCRA metals. More specifically, for each individual waste stream plus soil, fly ash and sodium/flux addition, variable leachability performances were observed. While both acetate buffer and acetic acid extraction fluids were prescribed per EPA's TCLP pre-extraction fluid determination procedure, the final pHs for the MTCLP leachates were generally between 5 and 8, with a single set of outliers at pH 11 for waste stream E with fly ash and high sodium/flux supplementation. The leachate performance of these formulations, characterized as they are by low final pHs and low metal leachate concentrations, highlight the successful fixation of the metals within the vitrified matrix. The MTCLP performance of the various formulations for uranium differ significantly. Uranium leached from waste streams A (11.4 mg/L), B (2.2 & 7.6 mg/L), C (3.98 & 5.72 mg/L), D (2.0 & 130 mg/L), F (1.81 & 45.9 mg/L) and G (1.3 & 1.7 mg/L) while waste streams E and H had non-detectable concentrations of uranium in the MTCLP leachate. It is proposed that the presence of acetate ions and the low final pH of the MTCLP leachate contributed partly to the soluble uranium concentrations observed.

Generally addition of fly ash or soil, as compared with vitrification of the waste without additives, decreased the leachability of uranium. There is an apparent trend that addition of fly ash gives lower leachability of uranium than with soil addition. Increasing sodium added with the fly ash generally increases the leaching of uranium. However, in three waste streams, addition of sodium with the soil samples dramatically decreased the leachability of uranium. None of the other metals leached in sufficient quantities to present a leaching problem. Barium was the only metal which leached in sufficient quantities to provide trends. Barium leaching in waste streams A through F supported the trend noted with the uranium leaching in which increased sodium loadings increased leaching. This trend was true with both fly ash and soil additions. In waste streams G and H, no barium leaching trends as a function of formulation could be established.

The 41 vitrification formulations performed fairly consistently during MPCT leach testing. No significant release of glass former target metals (e.g., aluminum at less than 9 mg/L; silicon at less than 30 mg/L and iron at ND) was observed except for waste stream E (using the "as-is" formulation) which had significant aluminum leaching (216 mg/L). Excluding the "as is" waste stream E sample, the flux metals typically leached less than 30 mg/L sodium, less than 13 mg/L potassium and less than 3 mg/L lithium; leaching of calcium ranged from 2 - 16 mg/L and magnesium from 0.02 - 16 mg/L without apparent pattern. In the case of the waste stream E sample, leaching of flux metals was significant: 126 mg/L sodium, 42 mg/L potassium and 8.4 mg/L lithium. These leachate values for former and flux metals for waste stream E indicate a poor quality glass in which the vitrified matrix is of low durability. The soluble uranium concentration for the MPCT leachates was ND in all cases. One possible explanation for this low leachability is that the final pH of the MPCT leachate was consistently in the high alkaline range, pH 10 - 11. Since this leachate was filtered at 0.45 micron prior to analysis

by ICP or ion chromatograph, insoluble alkaline uranium compounds would not be included in the leachate assay even if they had leached from the glass. Regardless, it should be noted in the case of the worst performing waste stream (E, "as is" formulation), the leaching of glass formers and fluxes was controlled when soil or fly ash supplementation was used.

The MPCT leachate results showed a trend of decreased leaching of metals and gross beta activity with the use of local fly ash when compared with glasses formed with local soil. The opposite trend was noticed for the gross alpha. This phenomena may be resolved with radioisotopic species identification in the leachate; however, that work was beyond the scope of this project. In addition, the higher sodium fluxed glasses tended to have higher metal leachate concentrations.

The Materials Characterization Center Static Leach Test (MCC-3) was developed for high level radioactive wastes and specified leaching test conditions with respect to waste form surface area and leaching solution volume. One of the outcomes of this test was a normalized leach rate (NLR) for waste constituents, expressed in $g/m^2/day$. The PCT leach test accommodates certain aspects of this test and defines a normalized leach rate for an abbreviated seven day leach period, specifying a limit of less than or equal to 1.0 $g/m^2/day$ as the performance standard for the leaching of any major glass constituent. Calculations were carried out using the compositional concentration of target metals compared to their concentration measured in the MPCT leachates to arrive at NLRs. Only waste stream E "as-is" formulation exhibited an NLR above 1.0 and that was for aluminum at 1.03. This particular formulation required a significant extra addition of sodium/flux to achieve processable viscosity and thus weighted the probability that the resulting formulation would favor enhanced matrix solubility.

CONCLUSIONS

Successful vitrification studies for eight low level radioactive waste streams were conducted. Durable glass formulations which were able to pass both the EPA's TC regulatory limits and the high level radioactive waste normalized leach rate criteria were determined. The effects of crucible materials of construction on the vitrified products were also observed.

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TREATMENT AND DISPOSAL OF A MIXED F006 PLATING LINE SLUDGE AT THE SAVANNAH RIVER SITE

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ABSTRACT. The Westinghouse Savannah River Company (WSRC), as the operating contractor for the Department of Energy (DOE) at the Savannah River Site (SRS) is implementing a program to treat and stabilize approximately 2800 m^3 of an F006 mixed (radioactive/hazardous) wastewater treatment sludge from electroplating operations. The uranium contaminated sludge resulted from nickel plating of depleted uranium targets, which were subsequently irradiated to produce plutonium for the weapons program. With the end of the "cold war", no virgin plutonium weapons production is forecast, and only the current SRS inventory of stored mixed plating line waste must be treated and disposed. A Life Cycle Cost analysis was used by WSRC to determine that the most cost effective approach was to treat the waste by a hazardous waste management sub-contractor, in a one time campaign. The analysis indicated that approximately 40 million could be saved by this approach, vs. the original plan to construct a permanent SRS treatment facility. The sub-contractor will mobilize treatment equipment on site, treat, stabilize, and place the final wasteform in disposal containers. The stabilized waste will be disposed to on-site SRS disposal vaults. This new approach also required a re-negotiation of a federal facility compliance agreement between the DOE and the Environmental Protection Agency.

INTRODUCTION

The end of the Cold War has caused major changes in the entire DOE weapons complex. A direct result of the reduced need for weapons production has been a re-evaluation of the treatment program for mixed (hazardous/radioactive) wastes generated from metal finishing and plating operations at the Savannah River Site (SRS). With the elimination of virgin plutonium production, generation of nickel plating waste was eliminated. Therefore, only the wastewater treatment sludge stored from past plutonium target production in the Reactor Materials Department (M-Area) needs to be treated. A Life Cycle Cost (LCC) analysis determined that the stored waste could be treated much more cost effectively in a one-time campaign by a hazardous waste treatment sub-contractor than by constructing permanent on-site facilities to treat the waste.

The M-Area plating line slurry resulted from the wastewater treatment of dilute rinsewaters from nickel electroplating and aluminum cladding operations. The dilute rinsewaters were neutralized and the precipitated heavy metals were removed by filtration using diatomaceous earth or perlite filter aids. The filtercake was then combined with concentrated plating line bath residuals and stored in interim status RCRA storage facility tanks. The resulting slurry was a "listed" F006 mixed (hazardous/radioactive) waste, containing depleted uranium.

The nickel plating and aluminum cladding operations prepared depleted uranium targets for irradiation in the SRS reactors. The uranium cores were etched, cleaned, nickel plated, clad in aluminum, inspected, and steam autoclave pressure tested. The targets were then transferred to the SRS reactors for irradiation, where the neutron flux transmuted the uranium-238 to plutonium-239. The ^{239}Pu was separated from the uranium

targets in the SRS "canyons" and transferred to other DOE sites for weapons production. In 1985, depleted uranium targets were being irradiated in four SRS reactors, resulting in the generation of approximately 2000 m^3 of F006 plating line wastewater slurry per year in M-Area.

The original program to treat the M-Area wastewater slurry was conceived in 1985, with the expectation that the slurry would be treated in an on-site hazardous waste treatment facility. The M-Area Waste Disposal Facility (designated "Y-Area") was designed to treat 4500 m^3/yr. (1,200,000 gals/year), based on 2000 m^3 of continuing waste generation per year, and a 10 year work-off of the ~20,000 m^3 of waste that would be stored in tanks by 1994. An additional 950 m^3/year of blowdown from an on-site Consolidated Incinerator Facility was also scheduled to be treated by Y-Area. The Y-Area Facility design was based on the design of the SRS cementatious facility (designated "Z-Area") to treat the low-level radioactive salt-supernate from the SRS saltcake storage tanks (waste from SRS canyons). The Z-Area facility uses a Portland cement/blast furnace slag/flyash mixture as a stabilizing agent for the salt-supernate, resulting in a grout mixture which is pumped to above ground radioactive disposal vaults. The salt-supernate is a mixed waste (radioactive/ characteristically hazardous), but the final grout is non-hazardous, as the grout passes the Environmental Protection Agency's (EPA) Toxicity Characteristic Leaching Procedure (TCLP) for hazardous constituents.

SEPARATION AND TREATMENT OF THE SUPERNATE FROM THE M-AREA SLUDGE

The waste slurry stored in the M-Area Interim Treatment/Storage Facility (IT/SF) tanks has spontaneously separated into a supernate and sludge (~25% by volume). It was demonstrated that the supernate could be treated in the close-coupled M-Area Dilute Effluent Treatment Facility (DETF) using metal phosphate precipitation and enhanced filtration methods. A modification to the industrial wastewater permit for the DETF was approved by the South Carolina Department of Health and Environmental Control (SCDHEC) and treatment of supernate began in May, 1990. This resulted in a 65-75% reduction of the final volume of hazardous waste that will have to be treated, stabilized, and disposed by hazardous waste treatment and disposal facilities. The remaining sludge has a density of approximately 1.24 gm/cc and is about 36 wt. % solids (after drying at 100°C). The approximate dry weight composition of the sludge is as follows:

Main Constituents	Approximate % Molar concentration
$Al(OH)_3$	26
$NaNO_3$	22
SiO_2 (amorphous)	31
Ca zeolite (residual filter aid)	3
$AlPO_4$	6
Uranium (sodium uranate)	7
$Ni(OH)_2$	1

TREATMENT AND DISPOSAL STUDIES ON M-AREA SLUDGE

Delisting Petition Study

A series of treatability studies were conducted by M-Area and the Savannah River Technology Center (SRTC) in 1988, to support a Delisting Petition for the stabilized sludge. The tests were conducted using sludge samples from the M-Area IT/SF tanks and the Y-Area process and stabilization materials. The final product was tested by both the EPA Extraction Procedure for Toxic wastes (EP Toxic) and the Toxicity Characteristic Leaching Procedure (TCLP). The final wasteform did not meet the 0.32 mg/L nickel leachant criteria promulgated by the EPA as the Best Demonstrated Available Technology (BDAT) for F006 "listed"

plating wastes (Table 1). None of the other constituents of concern for plating line sludges (Cd, Cr, Pb, Ag, or CN) were used in the M-Area plating operations.

Table 1. Initial Test Results for Delisting vs. EPA Land Ban Criteria.

	Maximum For Any Single Grab Sample		
Constituent	LDR Standard*	Delisting Petition - Tank 8 Sample Results	
	TCLP (mg/L)	TCLP (mg/L)	EP Toxic (mg/L)
Cd	0.066	<0.01	<0.01
Cr	5.2	<0.05	<0.05
Pb	0.51	<0.10	0.2 - 0.3
Ni	0.32	0.030-0.81	1.2 - 2.0
Ag	0.072	<0.01-0.04	<0.05

* LDR = Land Disposal Restrictions

Sludge Pretreatment (Filtration) and Stabilization Study

Based on the results of the initial treatability study, a series of filtration tests were conducted in November, 1988 and March, 1989. The objective of these filtration tests was to determine how to treat the wastewater slurry (filtercake plus concentrated tank residues) from continued production of depleted uranium targets in M-Area. Also, the sludge remaining in the IT/SF tanks after the supernate was decanted would be treated by the same filtration process. The pilot filtration program included a number of formulation and stabilization tests to improve the leaching durability of the final wasteform, so that the Land Disposal Restriction regulations for hazardous waste leaching requirements could be met.

The tests demonstrated that pressure filtration of the slurry, followed by pressure washing/rinsing of the filtercake, reslurring with water, and mixing with the Y-Area dry solids mixture (or with Portland Type II cement) would produce a final stabilized wasteform which met the Land Ban Restrictions leaching criteria for nickel. A high (~6:1) ratio of cement/blast furnace slag/flyash (or just cement) to the total solids in the M-Area sludge was used. This resulted in a large volume increase (~3.3X) from the initial waste to the final wasteform. The formulations and TCLP leaching results are summarized in Table 2. Only nickel, uranium, and nitrate were analyzed in the TCLP leachants, as the previous study had shown that the other F006 constituents would meet the BDAT criteria if nickel did.

These results indicated that either new M-Area slurry generated from on-going production, or the sludge remaining after supernate treatment could be washed, filtered, reslurried, shipped to and treated in the M-Area Waste Treatment Facility (Y-Area) to meet the LDR treatment standard for nickel. Cement alone, with or without additional sodium hydroxide, achieved the lowest nickel and uranium leachant concentrations, but the BFS/FA/cement mixture with additional NaOH was also acceptable.

Table 2. Sludge pretreatment formulations and TCLP leaching results.

	Formulation, Weight %			
Formulation	A	B	C	D
Sludge	6	6	6	6
BFS/FA/Cement*	52	47	-	-
Portland cement	-	-	52	47
NaOH	-	5	-	5
Water	42	42	42	42
	TCLP Leachant Concentration, mg/L**			
Nickel	<0.05 - 0.40	<0.05 - 0.21	<0.05	<0.05
Uranium	0.6 - 36	<0.2 - 16	<0.2	<0.2
Nitrate (as N)	0.5 - 3.0	0.4 - 3.2	0.2 - 1.4	0.5 - 2.6

*Blast Furnace Slag/Flyash/ Type II Portland Cement (45/45/10 dry wt.% ratio)

** Twelve separate tests for each formulation (different rinse volumes, with or with-out pre-neutralization of the sludge, and Ca, Mg, or Fe additives)

Stabilization of M-Area Sludge Using Cement and Pressure Filtration

A third treatability study was conducted by Savannah River Technology Center (SRTC) and M-Area in 1991. The objective was to determine if cement could be added directly to the sludge - prior to washing and pressure filtration - such that the final filtercake would meet the LDR restrictions without reslurring and additional processing. Scouting tests in the previous study had indicated that this approach could also provide substantial volume reduction of the final wasteform.

The sludge feed for the filtration tests was prepared by adding Portland Type II cement to the sludge, at a ratio of 1 gm cement to 4 gm total suspended solids (TSS). The sludge density was 1.24 gm/cc, with a TSS of 24 wt.%. The weight of the dissolved sodium nitrate (~12 wet wt. %) was not considered, since most of the sodium nitrate was removed during the filtration and cake washing operations. The cement/sludge mixture was filtered in a 0.041 m^2 (0.45 ft^2) Filtra-Systems Verti-Press® pilot scale filter, at a feed pressure of 2.7 x 10^5 Pa (25 psig) and a dewatering squeeze pressure of 8.3 x 10^5 Pa (105 psig). Water was added to the filter press, and again pressure filtered, to wash the cake. The results of the feed rates and filtration rates were used to determine the design specifications for a full scale filtration unit, with the capability to support continued production and work-off of the stored sludge. The following variables, and ranges, were evaluated:

- Weight ratio of cement to sludge solids — 0, 0.13, 0.27, 0.40
- Volume ratio of wash water to slurry feed — 0:1, 1:1, 2:1
- Use of cationic polymer (Praestol ® K110L) — 0 to 18 mg/L
- Ratio of filter aid (Envirogard®) to sludge solids* — 0, 0.13, 0.27
- Ratio of $Ca(OH)_2$ to sludge solids* — 0, 0.13, 0.27

*without cement addition

The key test combinations and TCLP results are summarized in Table 3.

Table 3. Direct cement addition test conditions and leaching results.

	Conditions								
Test No	11	4	7	2	1	26	34	33	32
Feed volume, L	1	2	2	2	2	2	2	2	2
Wash volume, L	1	2	2	2	0	2	2	2	2
Sludge solids, gms	294	588	588	588	588	588	588	588	588
Cement, gms	0	79	157	236	157	157	0	0	0
Ratio, cement to solids	0	0.13	0.27	0.40	0.27	0.27	0	0	0
Polymer	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
Filter aid, gms	0	0	0	0	0	0	0	79	157
$Ca(OH)_2$, gms	0	0	0	0	0	0	157	79	0
Final filtercake vol., L	0.3	0.8	0.7	0.4	0.8	0.8	0.8	0.8	0.7
	TCLP Leach Results, mg/L								
Nickel	2.9	0.14	<0.05	0.18	0.14	<0.05	<0.05	0.08	0.63
Uranium	74	1.9	0.7	0.9	1.3	<0.02	11	31	22
Nitrate, (as N)	27	11	9.7	9.5	300	11	55	21	9
TCLP pH	6.0	8.2	9.3	8.7	8.2	9.6	9.0	9.1	7.0

The key conclusions from the direct cement addition, plus pressure filtration and cake washing, were:

- Cake washing is required to provide a nitrate level in the final leachant which would support a delisting petition (test No. 1, without rinsing, had 300 gm/L in the TCLP leachant).
- All of the tests using cement resulted in a nickel concentration of less than the LDR standard of 0.32 mg/L in the TCLP leachant.
- The lowest uranium leachant concentration (<0.02 mg/L) was observed without polymer.
- Uranium concentrations of ~1 mg/L were observed with cement and polymer.
- Uranium leachant concentrations were ~10X higher without cement (tests 32,33,34)
- The lowest nickel concentrations were highly correlated with the measured pH of the final TCLP leachant solution.
- All of the tests resulted in a final volume of approximately 1/2 (or less) of the original sludge volume.

M-AREA FILTRATION AND STABILIZATION FACILITY (FIST)

The second treatability study in 1989 had demonstrated that if the M-Area sludge were filtered, washed, and reslurried prior to transfer to the Y-Area facility, the final Y-Area product would meet the LDR treatment requirements. The third study demonstrated that if cement were added directly to the sludge prior to filtration and washing, a filtercake could be produced which met the LDR requirements and did not require additional treatment.

Based on the results of the treatability studies, the functional design criteria were established for a Filtration and Stabilization (FIST) facility in M-Area. The facility was to:

- Treat nickel plating sludge from continuing target production in M-Area and/or to treat the sludge from the IT/SF tanks remaining after supernate treatment. The filtered and washed filtercake could be either:
  1) Reslurried and transferred to the centralized Y-Area for final treatment and disposal, or
  2) Transferred directly to the on-site Hazardous Waste/Mixed Waste (HW/MW) disposal vaults.

The FIST facility was estimated to cost approximately $12 million in capital funds, and approximately $2 million/yr in operating costs.

Volume of waste to be treated

In 1991, the Department of Energy-Savannah River (DOE-SR) directed WSRC to change the status of the Building 313-M Slug Production Process, the facility in which the nickel plating operations were conducted, from "standby" to "shutdown". The production of virgin Pu239 was not anticipated prior to the year 2000, if at all. The formal cessation of plutonium production was announced by the Bush administration a year later.

This meant that no new plating line slurry would be generated for treatment, and that only the stored sludge remaining (after treatment of the supernate from the IT/SF tanks) would have to be treated and stabilized. The total amount of sludge to be stabilized in 1995 was estimated to be approximately 2,700 m^3. This would result in a 270 m^3/year treatment rate, assuming a 10 year work off by Y-Area, or by the FIST direct filtercake process.

However, since the FIST facility was not needed to support on-going operations in M-Area, and would only be needed to pretreat the stored sludge prior to shipping to Y-Area, the necessity for the FIST facility was questioned. A Life Cycle Cost (LCC) analysis was conducted by the WSRC Systems Engineering Department to determine the most cost effective approach to manage the stored F006 sludge.

LIFE CYCLE COST ANALYSIS FOR TREATMENT OF THE M-AREA SLUDGE

Three cases were studied:

A. The sludges were pretreated and reslurried in the M-Area FIST facility, shipped to Y-Area, stabilized with BFS/FA/Portland cement, and disposed as a grout in the Y-Area vaults. The volume of the final grout was assumed to be 2x the volume of the original sludge.
B. The sludges are pretreated and stabilized in the M-Area FIST facility, and then shipped to the Hazardous Waste/Mix ed Waste (HW/MW) vaults for disposal. This case assumed a 50% volume reduction for the final wasteform vs. the initial sludge volume (75% reduction vs. case A), by adding Portland cement to the sludge prior to the high pressure filtration step. Disposal in the HW/MW vaults is more expensive on a volume basis (vs. the Y-Area vault), due to the higher cost of the HW/MW vaults ($ 6 million vs. $ 4 million) and a lower loading factor (drums or boxes vs. full pour of grout).
C. The third case assumed that a hazardous waste subcontractor would stabilize the sludge in M-Area, place in containers, and dispose in the HW/MW vaults. A 2X volume increase from sludge to final cementatious wasteform was assumed in this case.

Results of Life Cycle Cost Study

The Life Cycle and Present Worth Cost estimates for Case A included the capital and operating costs for the M-Area pretreatment facility, a prorated share of the operating cost at Y-Area, and the capital cost for the Y-Area vaults. The estimated Life Cycle Cost saving of $20 million for Case B vs. Case A resulted

from the lower volume of final waste (even including the higher cost of the HW/MW vaults and the lower loading factor vs. the Y-area vaults), and no operating cost for Y-Area to treat M-Area sludge. The contractor option (Case C) indicated a significant opportunity for an additional $20 million cost saving (vs. case B). The cost saving for this option resulted primarily from eliminating the capital cost for the pretreatment facility in M-Area ($12 million) and eliminating the operating costs for the pretreatment facility over the 10 year work-off period ($2.4 million/year). The total estimated cost saving for the contractor option vs. the Y-Area option was $40 million.

Based on this cost study, WSRC recommended to the DOE-SR that the contractor option be selected, that design and construction of the pretreatment (FIST) facility be canceled, and that the M-Area wastes not be shipped to and treated/disposed in Y-Area.

The results of the M-Area LCC cost study are summarized in Table 4.

Table 4. Case descriptions and LCC and PW costs.

Case	A	B	C
	Pretreat in M-Area, stabilize & dispose in Y-Area vaults	Pretreat and stabilize in M-Area; dispose to HW/MW vaults	Contractor stabilize in M-Area; dispose to HW/MW vaults
		Costs, $ x 10^6	
Capital			
M-Area	10	12	-
Y-Area*	1	-	-
Trucks	2	-	-
Start-up **	1.6	1.1	-
10 year operating			
Y-Area***	20	-	-
M-Area	18	24	-
10 year vault space (including boxes)	4.3	2.3	12
Contractor fee (at $0.033/m^3)	-	-	6.3
Contractor Project administration	-	-	2.2
Clean closure of all IT/SF tanks	-	-	2.5
Life Cycle Cost (LCC)	67.7	46.4	28.2
Present Worth (PW) Cost	53.6	37.7	22.0

* incremental capital costs for storage tanks in Y-Area

** includes FIST and partial Y-Area start-up costs

*** 25% of Y-area annual operating costs, based on relative volume of M-Area sludge to CIF blowdown

Life Cycle Cost Analysis Procedure

Assumptions. The following assumptions were used:

- 2725 m^3 of sludge to be treated
- HW/MW vaults cost $6 million each
- HW/MW vaults will hold 9000, 208 L (or 268 L square) drums each, (2400 m^3), or
- HW/MW vaults will hold 1200 B-25's (2.6m^3/B-25 = 3100m^3)
- Y-Area vaults cost $4 million each, with a capacity of 5140m^3.
- Average labor rate = $44.50/hr.
- Start-up costs = 25% of 1st year operating cost + 5% of capital cost.
- Life cycle and present worth costs based on 10 year operating life, with no salvage value.
- The economic analysis is intended to compare the relative costs of the different cases, and is not intended to be a definitive cost estimate of the actual life cycle cost.
- Final wasteform(s) will meet the Land Disposal Restrictions TCLP leaching criteria.
- Stabilization of the sludge by cementatious stabilization will result in 2X volume increase.
- Wastewater treatment will provide effluents which will meet NPDES permit requirements.

Economic evaluation analysis method. The Life Cycle Cost (LCC) and Present Worth (PW) were calculated using the following definitions and formulae (1, 2):

- LCC estimating is anticipated costs directly and indirectly related to preoperational, operational, and terminal stages.
- PW is a discounted dollar value, based on a technique of converting various cash flows occurring over a long period of time to equivalent amounts at a common point in time -- to facilitate a valid comparison.

$$LCC = (CC + SU) + (ECF * Y) + (ECF * Q) \quad (1)$$

$$PW = (CC + SU) + \{ Y * [(\frac{(1+i)^{N-1}}{(i \times (1+i)^N)}) + D] \} + Q * \{ Y \times [(\frac{(1+i)^{N-1}}{(i \times (1+i)^N)}) + E] \} \quad (2)$$

CC = Capital Cost
SU = Start-Up cost
ECF = Escalated Cost Factor for 10 years = 12.6
Y = Yearly operating cost
D = Operating cost escalation gradient factor, over 10 years (1.58)
N = Number of operating years (10)
i = Discount rate (5%)
Q = Annual Vault cost
E = Vault cost escalation gradient factor, over 10 years (1.31)

The PW calculation is primarily based on the initial capital investment and startup costs of the facilities, while the LCC reflects the escalated costs for the continuing capital expenditures for disposal vaults and continuing operating expenses. It is the authors' opinion that the LCC analysis provides a better comparison of the relative long term costs of the three cases than does the PW calculation, due to the continuing cost of providing disposal vaults on an ongoing basis.

LAND DISPOSAL RESTRICTIONS - FEDERAL FACILITIES COMPLIANCE AGREEMENT (LDR-FFCA)

There was another hurdle to be overcome before the new contractor option could be implemented. The M-Area sludge is a RCRA listed waste and a portion of the sludge was a "California List" waste, since it had been "actively managed" after July 1987, and had a concentration of >134 mg/L of nickel in the liquid from the sludge. The DOE-SR and WSRC had negotiated a Land Disposal Restrictions - Federal Facilities Compliance Agreement (LDR-FFCA) with the Environmental Protection Agency-Region IV in January 1991. The LDR-FFCA between the DOE and the EPA specified a number of activities which would be conducted by specific dates. The specific activities included submission of complete permit applications for Y-Area facility and the M-Area Pretreatment Facility. Construction of both facilities within specific time periods after the permits were approved was specified in the FFCA, and treatment goals were to be defined when operations commenced. The existing LDR-FFCA therefore had to be modified to remove the Y-Area and M-Area Pretreatment facility permit and construction deadlines, and replace them with new goals for the vendor treatment program. The EPA approved the LDR-FFCA modification request in April 1992, primarily because the new vendor treatment approach allowed the treatment of the M-Area sludge to start about one year sooner than the original Pretreatment plus Y-Area concept (Case A), and treatment of the M-Area sludge would be completed approximately ten years sooner.

SUMMARY

With the end of the plutonium target production at the Savannah River Site, the need for an on-going facility to treat newly generated and/or a stored mixed waste sludge was re-evaluated. A Life Cycle Cost analysis indicated that an estimated saving of $40 million could be realized by eliminating the planned Pretreatment (FIST) facility and instead to the waste treated and stabilized by a hazardous waste sub-contractor (in a one time campaign). The sub-contractor is to mobilize the equipment and personnel on site, treat and stabilize the waste, and place it in seventy-one gallon square drums (or equivalent). The drums will be transferred to WSRC, who will provide interim storage and final disposal. The contractor will be responsible for certifying that the final waste meets the WSRC waste acceptance criteria, and reworking any waste that does not. WSRC has specified acceptance criteria which should allow a delisting petition to be approved by the EPA. WSRC will be responsible for the sample analysis, preparation, and submission of the delisting petition. If the delisting petition is approved by the EPA, this will allow the disposal of the stabilized waste to low level radioactive disposal vaults, rather the much more expensive RCRA hazardous waste disposal vaults.

This change in the SRS program to treat and dispose of hazardous/radioactive wastes at the Savannah River Site exemplifies the commitment of the Westinghouse Savannah River Co. to provide the most cost effective management possible for the DOE challenges of the 90's.

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SOLIDIFICATION RESULTS FROM A TREATABILITY STUDY OF NONINCINERABLE LOW-LEVEL MIXED WASTES

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ABSTRACT. The focus of this work is the bench-scale solidification of nonincinerable, land disposal restricted low-level mixed waste at the Idaho National Engineering Laboratory. The waste forms included: liquids, sludges, and solids; where the treatment techniques included the use of conventional hydraulic systems (e.g., Portland cement) and sulphur polymer cement. Heavy metals were the primary toxic constituents of concern, most notably mercury, lead, and cadmium.

Over 100 small monoliths were formed to solidify approximately 22 kg of low-level mixed waste. Optimum concrete formulations were derived for each waste, as based on toxicity characteristic leaching procedure (TCLP) analyses and a free liquids test. Results indicate that the waste loading in the concrete can be relatively high (waste to dry PC = 0.5 to 0.6) while the monolithic mass yields excellent TCLP results. The most favorable amount of water in concrete was determined to be 30–33% by weight. The results of this bench-scale study will find applicability at facilities where mixed or hazardous waste solidification is a planned or ongoing activity.

INTRODUCTION

This paper covers the solidification of nonincinerable, land disposal restricted (LDR) low-level mixed waste generated at the Idaho National Engineering Laboratory (INEL). The objective of this document is to discuss the bench-scale solidification of samples of this mixed waste, which was done under a Resource Conservation and Recovery Act (RCRA) treatability study. Solidification was performed on several INEL wastes, where the treatment techniques included the use of conventional hydraulic-type cements (e.g., Portland cement) and a thermoplastic-type cement (sulphur polymer cement, SPC). Waste forms included liquids, sludges, and solids.

The ultimate goal of this work is to use appropriate solidification techniques (1, 20), to transform low-level mixed waste to low-level nonhazardous waste by satisfying pertinent disposal requirements for the treated waste. This work is meaningful in that it will provide a basis for the disposal of waste that is currently categorized as LDR low-level mixed waste.

WASTE DESCRIPTIONS

Waste Forms

The INEL mixed wastes that were investigated during this study are listed in Table 1; the waste generator, drum bar codes, and drum volumes are given. As this table indicates, most of these wastes are contained

in 55-gal drums. Table 2 contains a more qualitative description of the physical waste form, as gained from visual observation; nine mixed waste samples are listed. It should be noted that there is more than one type of waste form (solid, liquid, or sludge) for two of the INEL wastes. The Babcock & Wilcox (B&W) sludge listed in Table 2 is an additional waste that was not included in the original experimental design matrix; however, a small, six-monolith matrix was performed for this waste.

Waste Characterization Results

Early in this work,(3) it was decided that the information given on EG&G-669 forms (Generator's Hazardous Waste Material Profile Sheet) was insufficient to formulate a satisfactory characterization data base for the solidification of mixed waste. Thus, representative samples of the mixed waste given in Tables 1 and 2 were sent off site to undergo more analyses, namely toxicity characteristic leaching procedure (TCLP), percent moisture, and total dissolvable material (TDM) tests. In addition, radiochemical analyses were performed, where alpha, beta, and gamma-emitters were characterized for each mixed waste sample.

TCLP. TCLP is the criterion established by the U.S. Environmental Protection Agency (EPA) by which a sample is judged as hazardous or nonhazardous from a toxicity basis, and will be the primary focus of monolith analysis for this work. According to RCRA guidelines (Section 3), a waste is defined as having toxicity characteristic (TC) if a leachate of that waste contains a component(s) in an amount that exceeds a predefined limit. Hence, a waste sample is said to "fail" TCLP testing if the TCLP results indicate the presence of a TC component at a concentration that exceeds the RCRA limit for that component. For the majority of this study, the components of concern are heavy metals.

TCLP results for toxic metals in the untreated samples, as determined by TCT-St. Louis laboratories, are provided in Table 3. The significant result that is seen in this table is that only three of the wastes listed (waste codes 124, 157(a)-liquids, and B&W-sludge) have concentrations of a metal(s) that exceed the EPA limit, where mercury, lead, and chromium are the only metals that exceed their concentration limit. Thus, only these three wastes can be classified as hazardous as far as TC is concerned, and the remaining waste should be considered for reclassification as nonhazardous low-level waste. In addition, TCLP tests were done to check for semivolatile organic compounds, and the results indicate that concentrations of all such compounds are well below regulatory limits for the samples submitted for testing. Since semivolatile organics are not a concern for the untreated waste samples, TCLP analyses for these compounds were not performed on the treated waste samples.

Moisture. Percent moisture data are desired when a particular waste is to be solidified with a hydraulic cement, so that the total water content of the concrete monolith can be determined. In most instances, the percent moisture values obtained by TCT-St. Louis were verified by this study. All moisture data are given in Table 4.

TDM Results. The amount of dissolvable material present in a waste can impact the performance of a hydraulic cement used to solidify that waste. Generally speaking, TDM results are an indicator of the amount of electrolytes (salts) that are present in a waste. Most hydraulic cements do not perform favorably when there is a high salt concentration in the concrete matrix. TDM results for the wastes of interest are provided in Table 4. Note that TDM is different from total dissolved solids (TDS), which is typically reserved for liquids analyses.

Table 1. LDR nonincinerable mixed waste slated for solidification.[a]

INEL waste identification number	Waste description (generator)	Drum bar codes	Volume,[b] drums
124	TAN mercury concrete material (TAN)	560–563, 566, 573, 574, 577–582, 599–602, 624, 639–646, 681	27, 55 gal
128	Sludge with free liquids (TRA)	651, 652	2, 55 gal[c]
142	Radiation/lead-contaminated debris (PBF)	1472	1, 15 gal
153	Mercury-contaminated soil/sludge (TAN/IET)	556, 558, 559, 632, 658, 708–711, 922, 941	11, 55 gal
157(a)[d]	Warm waste pond sludge samples and debris (WEDF, TRA)	900–907, 1701	9, 55 gal
186	Solidified ash that failed test (WERF)	685, 686, 2759	1 B-25 bin 1, 85 gal 1, 55 gal

a. Inventory data for this table were taken from the WROC "Controlled Mixed Waste Stream History Table for Year 1991" (1).

b. "Volume" represents the internal volume of the container used to hold a given waste, and so may not be the actual waste volume. In many cases, the actual waste volume is much less than the indicated container size. The B-25 bin listed under waste 186 contains two 55-gal drums.

c. These drums contained several smaller glass and plastic containers, many of which were sampled.

d. Stream 157(a) is cross-referenced with WERF code identification number 23–91.

IET - Initial Engine Test (Facility)
PBF — Power Burst Facility
TAN - Test Area North
TRA — Test Reactor Area
WEDF — Waste Engineering Development Facility
WERF — Waste Experimental Reduction Facility
WROC — Waste Reduction Operations Complex.

Table 2. Waste form descriptions: nonincinerable LDR mixed waste.

INEL Waste Code	Description
124 (solids)	Moist solids with small bits of rock and gravel (generally ≤1/4in. (0.63cm) in size), and laced with larger pieces of white and gray clay-like material. This clay makes up roughly 20 to 35% of the waste by volume. Color: bulk material is brown/orange-brown. Approximate moisture content: 48% by weight.
128 (sludge)	Dark colored sludge with small pieces of rock, soil, and twigs. It was not easy to get representative samples of this sludge for the various monoliths. Color: bulk material is black. Approximate moisture content: 88% by weight.
128 (solids)	Light-colored, sandy-textured solid that appears somewhat crystalline or salt-like. Some grinding was required to reduce particle sizes. Contains small pieces of organic matter that looks like tiny plant roots. Dry. Color: bulk material is light-tan. Approximate moisture content: 2% by weight.
142 (solids)	Loosely packed gravel and rock, having an average particle size of 1/8 to 1/4 in (0.32 to 0.63cm). It resembles aquarium gravel, only the particles have a flint-like appearance. Color: bulk "wet" material is light-brown. Dried material has a low density of about 0.4 g/cc. Approximate moisture content: 49% by weight.
153 (solids)	Brown clay-like clumps covered/coated with a fine, brownish material that looks like ground-up peat moss. Approximately 60 to 80% of this mixed waste volume is clay-like material, and roughly 3 to 5% is small rocks. Moist material has a high density. May have to grind the clay clumps after they have undergone drying. Color: bulk material is dark brown. Approximate moisture content: 10 to 15% by weight.
157(a) (liquid)	Slightly amber, aqueous solution with brown-orange precipitate on the bottom of the waste container. The precipitate occupies ≤1% of the solution volume, and looks filmy/organic in form. Approximate moisture content: 98% by weight.
157(a) (solids)	Soil-like appearance; roughly 30% of the waste volume is small rocks or pebbles. Dry. Color: bulk material is gray to light-brown. Approximate moisture content: 2% by weight.
186 (solids)	Gray, ash-like material in chunks. The chunks contain black material (possibly ash that has not solidified properly). Had to grind this material to reduce the average particle size. The ground material was black/gray-black. Color: gray on exterior of particles (looks like old cement); black on the inside of the particles. Approximate moisture content: 20% by weight.
B&W chromate sludge	Dark (usually black) colored sludge containing very fine solids. Approximate moisture content: 85% by weight.

B&W — Babcock & Wilcox

Table 3. TCLP results for LDR low-level mixed waste samples prior to solidification (in µg/L).

Metals	INEL waste identification number								
	124 (solid)	128 (sludge)	128 (solid)	142 (solid)	153 (solid)	157a (liquid)	157a (solid)	186 (solid)	B&W (sludge)
Silver	42[a]	42[a]	42[a]	42[a]	42[a]	262	42[a]	42[a]	12.0[a]
Arsenic	140[a]	140[a]	140[a]	200	140[a]	665	140[a]	140[a]	120[a]
Barium	504	575	169	240	1,815	4,440	1,000	1,650	3,340
Cadmium	5[a]	94	5[a]	5[a]	211	208	9	5[a]	5[a]
Chromium	82	620	120	10[a]	10[a]	2,240	144	47	105,000[b]
Mercury	1,900[b]	0.15	0.1[a]	0.1[a]	95	920[b]	0.93	0.11	27.8
Lead	7,080[b]	425	100[a]	100[a]	100[a]	1,430	100[a]	2,930	246
Selenium	518[a]	518[a]	518[a]	518[a]	518[a]	518[a]	518[a]	518[a]	2[a]

a. This is a value at or below the shown detection limit for this metal. Detection limits for a given metal may vary according to the instrument detection limit (IDL) of analytical instruments used on a given set of samples.

b. This is a value that exceeds the EPA/RCRA disposal limit for this metal.

Table 4. Percent moisture and TDM results for LDR low-level mixed waste.

Parameter	INEL waste identification number								
	124 (solid)	128 (sludge)	128 (solid)	142 (solid)	153 (solid)	157a (liquid)	157a (solid)	186 (solid)	B&W (sludge)
Percent moisture (wt%)	49.4	87.8	1.6	49.0	10.5	98.0	2.2	20.2	85.0
Total dissolvable material (mg/gm)	6.0	5.3	940	76.3	2.4	—[a]	—[a]	119	—[a]

a. Sample not tested.

Radiological Analyses

Gamma ray, gross spectrometric alpha, and beta-emitter analyses of the mixed waste samples were performed by the INEL. Quantitative results are not given herein because the ultimate focus of this solidification study was to investigate the immobilization of toxic metals, not radionuclides, and since the treated waste under consideration will be disposed of as low-level radioactive waste. Generally speaking, the radioactivity of the MW samples was in the low pCi/g to low nCi/g range. Although there were some samples that contained transuranic components, their activity was sufficiently low to enable the waste samples to be classified as low-level mixed waste, not transuranic mixed waste. Quantitative radiological data has been summarized elsewhere (Table 1).

REGULATORY LIMITS FOR HAZARDOUS CONSTITUENTS

D-Listed Waste

The INEL mixed waste investigated in this work is considered characteristic hazardous waste because it is believed to possess one or more toxic characteristics, which are denoted by a D-listed EPA code. Being such, it must conform to EPA treatment standards (according to RCRA) before it can be disposed of as nonhazardous waste. A summary of the treatment standards for the toxic metals considered herein is provided in Table 5.

SOLIDIFICATION BACKGROUND

General Information

This bench-scale study used the technology screening performed in the references in Footnotes a and b (Table 3) as a basis for choosing solidification methods used on the aforementioned INEL waste samples. Summary information from these references is given in Tables 6-8. Early in this work, the solidification techniques provided in Table 6 were evaluated using the following seven selection criteria.

- Compatibility with waste pH
- Compatibility with waste moisture content (wet versus dry)
- Compatibility with waste heavy metals content
- Compatibility with waste organics content
- Compatibility with waste homogeneity
- Treatment cost per unit volume of waste
- Final waste volume (impacts disposal costs).

Table 5. EPA treatment standards for toxic metals.

Constituent	EPA limit (mg/L)
Silver	5.0
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Mercury	0.2
Lead	5.0
Selenium	5.7

These criteria were used for technology screening because they make the best use of the available waste characterization data, reflect the overall compatibility of a solidification technique with a given waste, and give a qualitative comparison of treatment and disposal costs.

Table 8 contains the recommended solidification techniques for the INEL wastes of interest, as obtained from the preliminary technology screening. The first and second choices are shown for each mixed waste. The results of this study indicate that hydraulic-type cements and sulfur polymer thermoplastic "cements" are the most feasible means of solidifying most of the mixed wastes considered herein. Although organic polymer systems are listed, they were not seen as practical for bench-scale applications. It should be noted that the actual, specific solidification treatments that are used may depend on the type of required pretreatment (e.g., segregation, pH neutralization, sorption of free liquids, drying), and the final choice of full-scale solidification treatments may certainly depend on the cost of pretreatment options.

Hydraulic Systems

Portland Cement. The Portland cement used for this work was a Type I and II, low alkali formulation produced by Ash Grove Cement West Incorporated, which came in 94-lb (42.6kg) bags. Approximately 130 lb (59kg) of this cement was required for the entire bench-scale solidification effort. This type of cement was used to solidify liquid, solid, and sludge waste samples.

Portland Cement Plus Sodium Silicate. Sodium silicate pentahydrate ($Na_2SiO_3 \cdot 5H_2O$) from Spectrum Chemical Manufacturing Incorporated [Item S1433, 25-lb (11.3kg) bucket] was used in some monoliths as an curing accelerator additive. This was done by adding enough of the pentahydrate salt to the concrete recipe to achieve a concentration of 8 wt% Na_2SiO_3. *Concrete* is defined here as the mixture of Portland cement, water, waste, and any additives.

Table 6. Candidate techniques for treatment by solidification.

Technique	Advantages	Disadvantages
Hydraulic cement-based systems For example: — Portland cement — Portland cement plus flyash — Portland cement plus sodium silicate — Portland cement plus lime — Lime plus flyash	• Low cost • Proven stability • Safe chemical ingredients • Simple equipment • Variety of formulations available • Low concentrations of some organic materials (e.g., oils) can be treated • Suited for wet waste	• Volume increase of final waste form • Mass increase of final waste form • Not well-suited for waste having high concentrations of salts and/or organic solvents
Polymerization systems	• Can have a small volume increase of final waste form • Very low permeability • Quick setting/hardening compared to typical cement-based systems • May be suited for waste containing water, organic solvents, or oils	• High cost • Some chemicals used are hazardous • Possible biodegradation • Possible attack by ultraviolet sources • Complex equipment compared to typical cement-based systems
Organic polymer thermoplastic systems	• Can have a small volume increase of final waste form • Very low permeability • Quick setting/hardening compared to typical cement-based systems • High strength	• High cost • Some chemicals used may be hazardous • Possible biodegradation • Possible attack by ultraviolet sources • Heating unit needed • Complex equipment • Not well-suited for wet waste
Sulphur polymer thermoplastic systems	• Able to incorporate high concentration of salts into final waste • Very low permeability • Quick setting/hardening • Less waste volume increase compared to typical cement-based systems • High strength	• Unproven long-term performance • Moderate to high cost • Heating unit needed • Complex equipment compared to typical cement-based systems • Not well-suited for wet waste

Table 7. Recommended solidification methods for various waste categories.

Waste category	Recommended solidification method(s)	References[a]	Recommended pretreatment
Dry waste:			
Ash	HC; TPMic (SPC)	4, 5, 8, 9, 10, Footnote a on page 1	Mix/blend
Soils	HC; TPMic (SPC)	4, 8, 9, 10, 12	Mix/blend
Powders/residues	HC; TPMic; P/C	2, 4, 6, 7, 13, 14	Mix/blend
Evaporator salts	TPMic (SPC); TPMac	4, 6, 8, 9, 10, 17	Dry; mix/blend
Nonhomogeneous	TPMac for large items; HC for smaller items	2, 4, 6, 7, 11, 17	Segregate if possible
Wet waste:			
Sludges	HC; ASet; PSet	2, 4, 6, 7, 16, 19, Footnote a on page 1	Adjust pH; mix/blend
Moist solids	HC; P/C	2, 4, 6, 7, 11, 12, 13, Footnote a on page 1	Mix/blend
Free liquids (aqueous)	HC; ASet; ASet II	2, 4, 6, 7, 11, 19	Adjust pH; ppt; mix/blend
Special waste:			
Organic-laden	PSet II; HC; P/C	4, 13, 15, 19	Mix/blend
Salt-laden	TPMic (SPC); ASet II; TPMac	6, 8, 9, 10, 19	Dry; mix/blend
Debris-laden	TPMac; TPMic (poly)	2, 3, 4, 6, 11, 17	Segregate if possible
Multi-hazard	HC; TPMac	2, 4, 6, 11, 17	Neutralize acids and reactives; mix
High-level, radioactive mixed	TPMac; Vit	17, 18	Primary containment

a. See Section 8, except where indicated.

ASet — Aquaset (Fluid Tech, Inc.)
ASet II — Aquaset II (Fluid Tech, Inc.)
HC — hydraulic cements (e.g., Portland cement)
P/C — polymer/copolymer systems
poly — organic polymer systems
ppt — chemical precipitation
PSet — Petroset (Fluid Tech, Inc.)
PSet II — Petroset II (Fluid Tech, Inc.)
SPC — sulfur polymer cement
TPMac — thermoplastic macroencapsulation
TPMic — thermoplastic microencapsulation
Vit — vitrification.

Table 8. Summary of recommended solidification techniques.

INEL waste identification number	Waste description	Recommended solidification techniques (top two choices)
124	TAN mercury concrete material	1. Hydraulic cement 2. Polymerization
128[a]	Sludge with free liquids	1. Polymerization 2. Sulfur polymer thermoplastic
142[a]	Radiation/lead-contaminated debris	1. Organic polymer thermoplastic 2. Sulfur polymer thermoplastic
153[a]	Mercury-contaminated soil/sludge	1. Sulfur polymer thermoplastic 2. Hydraulic cement
157(a)[a]	Warm waste pond sludge samples and debris	1. Sulfur polymer thermoplastic 2. Hydraulic cement
186	Solidified ash that failed test	1. Hydraulic cement 2. Polymerization

a. Waste may require segregation before solidification treatment.

Thermoplastic System (Sulfur Polymer Cement)

The sulfur polymer cement (SPC) used for this work sells under the trade name CHEMENT 2000, and arrived in bulk in a 55-gal drum. This material was in the form of flakes having a thickness of approximately 1/8 in. (0.32cm), and is composed of approximately 95% sulfur and 5% additives. SPC was used to solidify dry waste only; mixed waste samples typically had to undergo a drying pretreatment.

BENCH-SCALE EXPERIMENTAL CONSIDERATIONS

Sampling and Testing Schedules

Mixed waste drum sampling took place at the INEL Waste Experimental Reduction Facility (WERF) during April 1992(2). Solidification of the mixed waste samples started in June 1992 and continued through August. This three-month period encompassed the time needed for monolith formation, curing, initial inspection, duplication of specific monoliths (if needed), and the start of representative sampling of the cured monoliths. Leaching tests (TCLP) and other tests needed to satisfy disposal criteria were performed during August through November 1992.

Experimental Parameters and Design Matrix

Experimental Design Matrix. When considering the experimental design matrix for monolith formation, there are essentially two separate experiments: one for hydraulic cement and another for nonhydraulic (sulfur polymer) cement. Of the nine wastes listed in Table 2, seven were solidified with hydraulic cements and the remaining two were treated with SPC. The purpose of the matrix-based study is to determine the most effective monolith "recipe" for each of the waste types.

The number of monoliths that are produced during a treatability study should be minimized so that the time and money expended on laboratory analyses of the monoliths can be decreased, and so that the disposal requirements of failed monoliths will be diminished. In an effort to minimize the number of monoliths while maintaining satisfactory data, this bench-scale study used the method of fractional factorials as a statistical approach toward reducing the total number of monoliths produced.

There are two steps to setting up the study, which can be improved with the use of statistics. First, there is the experimental design, which (for each waste type) defines the number and nature of the treatments (combinations of factor levels or "recipes") to be used, and the number of replications for each treatment. Second, there is the process of obtaining and assigning specimens (experimental units) to these treatments, often called a sampling plan. The experimental design is the focus of this section.

The wastes assigned to the hydraulic cement part of the study are defined by INEL waste identification numbers 124, 128, 157a, and 186, according to the recommendations given in Footnote a(Table 8). A summary of the factors for the hydraulic cement portion of the study is provided in Table 9, where design factors A, B, and C are represented by cement formulation, total water content of concrete mixture, and waste to dry cement weight ratio, respectively. For the most efficient estimation of curvature effects, the levels of factor C have been equally spaced when possible. A value of 0.5 for factor C in Table 9 was used instead of 0.6 for liquids and sludges that had a very high water content, so that the waste to Portland cement ratio could be attained without exceeding the desirable percentage of water in the concrete.

Table 9. Factor descriptions for the hydraulic cement portion of the study.

Factor	Factor definition	Factor type	Number of levels	Factor levels	Level code
A	Cement formulation	Qualitative, fixed	2	Portland cement:	
				Without additive	-
				With additive	+
B	Total water content of concrete mixture	Quantitative, fixed	2	30% by weight	-
				36% by weight	+
C	Waste to dry cement weight ratio	Quantitative, fixed	3	0.20	1
				0.40	2
				0.60 (0.50)	3

The two wastes assigned to the nonhydraulic cement portion of the study are defined by INEL waste identification numbers 142 and 153. A summary of the factor for the nonhydraulic cement portion of the study is provided in Table 10. There are three possible treatments (recipes) for each waste type. The values for factor C in Table 10 that are in parentheses (0.15, 0.25, 0.50) were used for INEL waste code 142 because this waste had a low density (approximately 0.4 g/mL), resulting in a large volume of material per unit of mass of waste that had to be wetted by the SPC; thus, the ratio of waste to SPC had to be reduced to accommodate favorable mixing conditions.

Additional Solidification Not Included in Experimental Design Matrix. There was a small number of monoliths produced in addition to those made under the experimental design matrix. These additional monoliths solidified secondary end-of-process waste, such as rinsing waste generated during the cleaning of mixing equipment, and leftover sample material. The solidification results for these monoliths are given in Appendix B.

Technical Procedures

The chronological sequence of activities for bench-scale solidification of LDR mixed waste was as follows:

1. Waste sample retrieval
2. Pre-bench-scale waste characterization
3. Procurement of bench-scale equipment and materials
4. Laboratory preparation at TRA
5. Waste sample pretreatment
6. Waste sample monolith formation and curing
7. Analysis of monoliths (e.g., TCLP, free liquids)
8. Interpretation of results
9. Interim storage of monoliths
10. Disposal of monoliths.

Table 10. Factor description for the nonhydraulic cement portion of the study.

Factor	Factor definition	Factor type	Number of levels	Factor levels	Level code
C	Waste to SPC weight ratio	Quantitative, fixed	3	0.25 (0.15)	1
				0.50 (0.25)	2
				0.75 (0.50)	3

Pretreatment of Waste Samples. Waste pretreatment may include one or more of the following: segregation, drying, mixing, neutralization, flocculation of free liquids, surfactant addition, etc. Pretreatment may be necessary to make a waste more compatible with a given solidification technique by increasing waste homogeneity and through canceling the inhibitive effects of particular waste constituents (e.g., acids, salts, or organic solvents). For this bench-scale study, pretreatment was primarily comprised of segregation/screening, size reduction of larger particles, mixing, and drying, and depended on the waste type and planned solidification treatment.

Segregated material larger than 1/2 in. (1.3cm) that was representative of a given waste sample (dirt clods or clumps, rocks, etc.) was reduced in size by crushing it with a mortar and pestle. Mixing of the sample material prior to solidification was typically done in the original sample container or in a glass or plastic beaker. Drying of sample material was accomplished by placing the material in a large beaker or an aluminum-lined tray, which was then set on a hotplate overnight. The degree of dryness was checked by noting the weight change of the sample per unit of time.

Pretreatment was not treated as a systematic test parameter; however, it was viewed as an important consideration in the overall solidification process. Table 10 contains the pretreatment steps that were performed for each of the wastes listed in Table 2.

Laboratory Procedures. The methodology for this work involves the use of straightforward solids-handling and solidification techniques for low-level mixed waste, which includes sample retrieval and transport, waste pretreatment, monolith formation, monolith sampling, monolith storage, and monolith disposal. Since sample retrieval, transport, and sampling were done by auxiliary personnel other than the author, these tasks will not be discussed in this document.

Bench-scale solidification was accomplished under controlled, supervised, and monitored conditions. The monoliths were formed inside containers (casts) that have an internal volume of approximately 1 L. For hydraulic-type concretes, monolith containers were made of high-density polyethylene (HDPE), whereas metal casts were used for SPC concretes. The use of metal containers is recommended for thermoplastic systems because of the higher temperatures that are encountered.

Table 11. Pretreatment of the wastes in Table 2.

INEL waste identification number	124 (solid)	128 (solid)	128 (sludge)	142 (solid)	153 (solid)	157a (liquid)	157a (solid)	186 (solid)	B&W (sludge)
Segregation/screening	X	—	X	—	X	—	X	X	—
Size reduction	X	—	X	—	X	—	—	X	—
Drying	—	—	—	X	X	—	—	—	—
Mixing/blending	X	X	X	X	X	X	X	X	X
pH adjustment (raise pH to ≥7)	—	—	—	—	—	—	—	—	X
Precipitation of free metals	—	—	—	—	—	—	—	—	X
Surfactant addition	—	—	—	—	—	—	—	—	—

Solidification took place in situ, where the cement and waste were mixed and cast in the same container, forming a homogeneous concrete mixture. This practice helped to reduce waste generation during bench-scale studies. Mixing procedures for hydraulic and non-hydraulic systems are given below.

Hydraulic-Type Cements. These type of cements were used first since they require the longest curing time, which is usually at least 28 days for a "full" cure. The primary concern for these type of systems is

attaining the optimal ratios of water to total solids and waste to cement. Although the literature gives some guidance for these ratios, optimal values are sometimes derived through trial and error.

For hydraulic systems, the general mixing procedure is summarized as follows. First, predetermined amounts of dry Portland cement and sodium silicate (if specified in the recipe) are weighed into a monolith container and mixed. Next, an appropriate amount of water is added to the container, and the resultant mixture is mixed by hand two to three minutes to an even consistency. A measured amount of each waste is then incrementally added to the cement mixture in the container while it is being mixed thoroughly with a heavy-duty laboratory stirrer. The entire concrete mixture is then mixed with the laboratory stirrer at 150–250 rpm for approximately 8 to 10 minutes. The procedure is finished by sealing the container, and then labeling and storing the container for the curing phase. All monolith containers were sealed with parafilm to minimize the evaporative loss of water.

Sulfur Polymer Cement. Since SPC literally cures "overnight," its use was scheduled after the hydraulic cements. SPC handling and mixing procedures are provided in Appendix A. For large-scale applications, the equipment required for the SPC system is anticipated to be the most complicated of the cements considered here, as it is likely to involve the use of a specialized heated mixing vessel and heated monolith casts. Additionally, there is more safety concerns tied to the sulfur polymer thermoplastic system because of the danger associated with the heated material, and the potential liberation of small quantities of hydrogen sulfide (H_2S) gas at temperatures exceeding 300°F (149°C).

Monolith Curing, Storage, and Disposal

Hydraulic concrete monoliths were allowed to cure at least 28 days before they were sampled. Monoliths made with SPC required only an overnight cure time, although there was typically at least a five-day period between SPC monolith production and sampling.

The overall storage requirements for the solidified monoliths are short term, which will be defined here as less than six months. Storage intervals can be described as follows:

- Storage during curing. Depends on the solidification system used. At least 28 days are required for most hydraulic systems to reach a "full" cure. However, it may be desirable to wait longer than 28 days for selected monoliths, since mechanical and chemical properties of hydraulic concretes generally improve with time.[4] Thermoplastic systems take far less time to cure than this.
- Storage during analyses (TCLP, etc.). Up to three months; this storage period depends on who will be doing the TCLP analyses and whether these analyses are performed on site or off site the INEL.
- Storage for those monoliths that failed analyses. Depends on how soon these monoliths can be re-treated, which has been estimated at less than six months from the time that the TCLP test results are determined.

The monoliths that pass the disposal criteria tests will be reclassified from LDR mixed waste to low-level nonhazardous waste. Treated waste that meets disposal criteria will be disposed of via a low-level waste disposal facility such as the Radioactive Waste Management Complex (RWMC) at the INEL. Those monoliths that fail to meet the disposal criteria will be kept in an approved temporary low-level mixed waste storage area, and re-solidified or encapsulated at a later date.

Scale-Up Considerations

One primary concern in scaling up the bench-scale methodology is to be able to duplicate the extent of mixing that was achieved during bench-scale work. Full-scale operations run the risk of not providing thorough enough mixing techniques to ensure that the concrete ingredients are truly homogeneous prior to the onset of the curing phase. Thus, an effort should be made to verify that intimate mixing is being achieved during full-scale mixing. The process notes given in the next section (Table 12) should be reviewed during the design of the full-scale system.

Another concern for scale-up is the containment of radioactive particles that could become airborne during routine waste handling operations. During bench-scale solidification, airborne particulate matter was controlled through the use of ventilation hoods. However, since ventilation hoods are impractical for full-scale systems, secondary containment will need to be seriously considered for full-scale solidification of the mixed wastes investigated herein.

RESULTS

General Observations

Overall monolith production for this project is summarized as follows. A total of 113 monoliths were made according to the experimental design matrix; 8 of these were "blanks" (contained no waste). Thus, 105 monoliths were used to solidify 21.6 kg of mixed waste; 92 were made with Portland cement systems, and 13 were made with SPC. In addition, there were a small number of additional monoliths that solidified supplemental waste not included in the design matrix, where the solidification results are discussed in Appendix B.

Of the wastes solidified during this study, two proved to be difficult to solidify, either during the mixing phase or the curing phase. These two wastes were INEL waste codes 128 (solids) and 142 (solids), and are discussed below.

INEL waste code 128 caused swelling in the Portland cement-based monoliths it was incorporated into; 2 of 15 monolith containers split because of the swelling. This may have been due to the high percentage of soluble solids that are present in this waste (Table 4). Perhaps the swelling could be avoided by using SPC instead of Portland cement. However, SPC is not compatible with some salts (especially oxidizers), so a chemical analysis should be performed to determine the predominant cations and anions in this waste. It should be noted that the Portland cement-based monolith recipes for this waste that included 8% Na_2SiO_3 did not swell as much as the monoliths using no added Na_2SiO_3.

INEL waste code 142 appears to be better suited for Portland cement systems than SPC. There are two main reasons for this. First, this waste is roughly 50% water, so it is time- and energy-intensive to dry it prior to solidification with SPC. If solidified with Portland cement, this mixed waste would require no pretreatment aside from mixing and blending. Second, the dried waste has a relatively low density (about 0.4 g/cc), which tends to make it float to the top of molten SPC. This floating problem could be eliminated by using a Portland cement system with a higher viscosity than molten SPC.

Table 12. Bench-scale process notes for nonincinerable LDR mixed wastes.

INEL waste code	Special process notes
124 (solids)	Because of the clay content (roughly 20–35% of waste is clay-like material), it is recommended that the waste be granulated to smaller than 1/4 or 1/2 in. (0.63 or 1.63cm) before solidification to decrease the size of the clay particles (as was done for bench-scale testing). This material is sometimes gummy, and mixing equipment should be self-cleaning if possible. The monolith formulation having the highest ratio of waste to cement and the lowest percentage of water was unworkable because of insufficient "free" water for mixing.
128 (sludge)	Because of the physical form of this waste (heavy solids in a liquid), process methods should be used that will prevent the solids from settling to the bottom portion of the concrete prior to curing. This can be accomplished by using upward mixing (moving material from bottom to top), and by using a concrete formulation that has a lower water content, which will result in a higher concrete viscosity. Because of the high moisture content of this waste (approximately 88% water by weight), some of the higher waste to cement ratios that were planned could not be attained without exceeding an upper limit of total percent water. This resulted in the deletion of 2 of 15 monolith formulations from the experimental design matrix.
128 (solids)	This mixed waste caused swelling of the monoliths that was incorporated into, most noticeably in monoliths having high percentages of both mixed waste and water. Two of the 15 monolith containers used for solidification of this waste split from the swelling. Since it is a high priority to choose concrete formulations that will not jeopardize the integrity of the containers that hold them, it is suggested that future monoliths made with this mixed waste be made with low percentages of mixed waste and/or low percentages of water. Also, this may be a good candidate for SPC if the mixed waste does not fracture the concrete matrices when it has opportunity to absorb water. This material had to be ground with a mortar and pestle to reduce the average particle size.

INEL waste code	Special process notes
142 (solids)	In hindsight, this waste would have been a perfect candidate for hydraulic-type systems rather than SPC. The relatively high moisture content of this material (approximately 49% water by weight) would have been acceptable for hydraulic concretes, where as it is a liability for SPC systems. Drying this mixed waste is both time- and energy-intensive, as it must be heated for a prolonged time (at least three to four hours for bench-scale applications). Another problem that arose was caused by the low density of this mixed waste, which caused it to rise to the top of the molten SPC; this problem could have been avoided by using a thicker, more viscous hydraulic-type cement.
153 (solids)	Because of the clay content (roughly 60–80% of waste is clay-like material), it is recommended that the waste be granulated to smaller than 1/4 or 1/2 in. (0.63 or 1.3cm) before solidification to decrease the size of the clay particles (as was done for bench-scale testing). This material is sometimes gummy, and may tend to clog or stick to process equipment if used with hydraulic cement systems; thus, such equipment should be self-cleaning if possible. If used with SPC, the material should be dried thoroughly before or after the granulation step.
157(a) (liquid)	Because of high moisture content of this waste (approximately 98% water by weight), some of the higher waste to cement ratios that were planned could not be attained without exceeding an upper limit of total percent water. This resulted in the deletion of 2 of 15 monolith formulations from the experimental design matrix.
157(a) (solids)	At least 25–30% of the volume of this mixed waste was composed of rocks and pebbles that were larger than 1/2 in. (1.3cm), which could not be processed through the bench-scale equipment. However, these larger rocks would not be a problem for full-scale solidification equipment. The low moisture content of this mixed waste (2% by weight) makes it a candidate for SPC.
186 (solids)	This material had to be ground with a mortar and pestle to reduce the average particle size.
B&W chromate sludge	No problems were encountered with the solidification of this mixed waste. It appears to be a good candidate for hydraulic-type cements.

In addition, INEL waste code 153, as sampled, contained a small amount of elemental mercury that apparently caused the solidified monoliths for this waste to exceed the RCRA limit for mercury. This elemental mercury was seen at the bottom of the container that was used to hold this waste during the drying pretreatment step, prior to solidification with SPC. Regardless of the full-scale solidification technique that will be used on this mixed waste, a pretreatment step should be used wherein the elemental mercury is effectively removed from the waste matrix. A gravity-based separation technique would be a good candidate for such a pretreatment step.

Process Considerations

Table 12 contains notes for each waste that detail difficulties or significant observations pertaining to the bench-scale processing of the waste listed in Table 2. These notes should be applicable to scale-up considerations.

TCLP Test Results

All waste-bearing monoliths were subjected to TCLP testing after they had undergone a curing period. TCLP data were generated by TCT-St. Louis Laboratories of St. Louis, Missouri.[20] Data validation and qualification will be performed according to project needs.

Of the waste codes listed in Table 2, three had toxic metals that exceeded their EPA/RCRA concentration limit [124-solids, 157(a)-liquids, and B&W-sludge], where mercury, lead, and chromium are the toxic metals of concern according to TCLP analyses of the raw waste. Table 13 contains the summary results for the TCLP analyses of the untreated and solidified monolithic waste material. The "After" results given in this table correspond to the concrete recipes (see recipe codes) that produce no free liquids, and that lower the leachability of toxic metals to the greatest extent while allowing the ratio of waste to Portland cement to remain high. Although their choice is somewhat subjective, those recipes indicated in Table 13 are the best recipes deduced by this study as far as leachability and free liquids are concerned.

The results in Table 13 indicate that solidification via Portland cement is a very effective means of immobilizing toxic metals, where monolith recipes having higher amounts of waste (waste/Portland cement=0.5 to 0.6) generally performed as well as those having lesser amounts (waste/Portland cement=0.2), using TCLP as a criterion. Such results infer that it may be possible to load the concrete with greater amounts of waste while passing TCLP tests and satisfying disposal criteria.

There were also a small number of monoliths that failed TCLP tests, wherein their concentrations exceeded the limits imposed by RCRA. Given the relatively broad experimental design matrix described in Section 5, it should not be unexpected that some of the monoliths would fail one or more disposal criteria. The monolith recipes that failed TCLP are given in Table 14, where three monoliths for waste code 153 failed TCLP for mercury, and three monoliths for waste code 186 failed TCLP for cadmium. The results seen in Table 14 are unusual in that the untreated wastes for INEL waste codes 153 and 186 passed TCLP by a good margin, and yet the treated wastes for these codes produced some monoliths that failed TCLP. Such results are unexpected and counter-intuitive, as there seems to be no clear explanation for them.

However, there are a few possible explanations for why some of the monolith samples for INEL waste codes 153 and 186 failed TCLP tests while the untreated wastes passed. First, the laboratory results or procedures for the analysis of the metals of concern could be in error. Second, the concrete ingredients may have caused a chemically favorable environment for the leaching of the indicated metals in Table 6-3. Lastly, the pretreatment step(s) used for INEL waste codes 153 and 186 may have altered the waste matrix and caused it to be more susceptible to the effects of leaching. Pretreatment of INEL waste code 153 involved drying the moist waste over a hot plate at 300–350°F (149 to 177°C) overnight, followed by size reduction to less than 1/2 in. (1.3cm) via mortar and pestle. INEL waste code 186 was pretreated by size reduction only. It is useful to note that all of the monolith recipes that failed TCLP for INEL waste code 186 contained added sodium silicate. The cause for the anomalous results in Table 14 should be found before full-scale solidification of these wastes is attempted.

Table 13. Best TCLP results (μg/L) for LDR low-level mixed waste samples.

Metal		INEL waste identification number								
		124 (solid)	128 (sludge)	128 (solid)	142 (solid)	153 (solid)	157a (liquid)	157a (solid)	186 (solid)	B&W (sludge)
Mercury	Before	1,900[a]	0.15	0.1[b]	0.1[b]	95	920[a]	0.93	0.11	27.8
	After	0.1B[b]	0.1[b]	0.1[b]	0.1[b]	85	0.1[b]	0.1[b]	0.1[b]	0.1[b]
	Recipe code	a	m	k	q	r	m	j	d	o
Lead	Before	7,080[a]	425	100[b]	100[b]	100[b]	1,430	100[b]	2,930	246
	After	22[b]	23	22[b]	22[b]	107	22[b]	78[b]	34	22[b]
	Recipe code	a	m	k	q	r	m	j	d	o

a. Indicates a value that exceeds the EPA/RCRA limit for that metal.

b. Indicates a value at or below the shown detection limit for that metal. Detection limits for a given metal may vary according to the instrument detection limit (IDL) of analytical instruments used on a given set of samples.

NOTE: "Before" and "After" are with respect to solidification treatment.

B&W results for Cr: Before = 105,000 μg/L; After = 19.0 μg/L. The RCRA limit for Cr is 5,000 μg/L.

Waste codes 142 and 153 were solidified with SPC.

Untreated samples of INEL waste codes 153 and 186 should be resubmitted for TCLP analysis.

Key of recipe codes (percentages shown are percent weight in concrete):

a = waste/Portland cement = 0.6; water = 36%; no added sodium silicate
b = waste/Portland cement = 0.4; water = 36%; no added sodium silicate
c = waste/Portland cement = 0.2; water = 36%; no added sodium silicate
d = waste/Portland cement = 0.6; water = 30%; no added sodium silicate
e = waste/Portland cement = 0.4; water = 30%; no added sodium silicate
f = waste/Portland cement = 0.2; water = 30%; no added sodium silicate
g = waste/Portland cement = 0.6; water = 36%; sodium silicate = 8%
h = waste/Portland cement = 0.4; water = 36%; sodium silicate = 8%
i = waste/Portland cement = 0.2; water = 36%; sodium silicate = 8%
j = waste/Portland cement = 0.6; water = 30%; sodium silicate = 8%
k = waste/Portland cement = 0.4; water = 30%; sodium silicate = 8%
l = waste/Portland cement = 0.2; water = 30%; sodium silicate = 8%
m = waste/Portland cement = 0.5; water = 36%; no added sodium silicate
n = waste/Portland cement = 0.5; water = 36%; sodium silicate = 8%
o = waste/Portland cement = 0.5; water = 30%; no added sodium silicate
p = waste/SPC = 0.75
q = waste/SPC = 0.50
r = waste/SPC = 0.25.

Table 14. Failed TCLP results (μg/L) for solidified mixed waste samples.

INEL waste code	Recipe code	Heavy metal concentration, μg/L			
		Mercury		Cadmium	
		Before	After	Before	After
153	p	95.0	737[a]	NA	NA
153	p	95.0	203	NA	NA
153	q	95.0	299	NA	NA
186	g	NA	NA	5.0[b]	5,895[a]
186	i	NA	NA	5.0[b]	1,200
186	j	NA	NA	5.0[b]	3,030

a.Indicates an average value derived from duplicate TCLP analyses.

b.Indicates a value at or below the shown detection limit for that metal. Detection limits for a given metal may vary according to the instrument detection limit (IDL) of analytical instruments used on a given set of samples.

NA — not applicable

NOTE: "Before" and "After" are with respect to solidification treatment.

Key of recipe codes (percentages shown are percent weight in concrete):

a = waste/Portland cement = 0.6; water = 36%; no added sodium silicate
b = waste/Portland cement = 0.4; water = 36%; no added sodium silicate
c = waste/Portland cement = 0.2; water = 36%; no added sodium silicate
d = waste/Portland cement = 0.6; water = 30%; no added sodium silicate
e = waste/Portland cement = 0.4; water = 30%; no added sodium silicate
f = waste/Portland cement = 0.2; water = 30%; no added sodium silicate
g = waste/Portland cement = 0.6; water = 36%; sodium silicate = 8%
h = waste/Portland cement = 0.4; water = 36%; sodium silicate = 8%
i = waste/Portland cement = 0.2; water = 36%; sodium silicate = 8%
j = waste/Portland cement = 0.6; water = 30%; sodium silicate = 8%
k = waste/Portland cement = 0.4; water = 30%; sodium silicate = 8%
l = waste/Portland cement = 0.2; water = 30%; sodium silicate = 8%
m = waste/Portland cement = 0.5; water = 36%; no added sodium silicate
n = waste/Portland cement = 0.5; water = 36%; sodium silicate = 8%
o = waste/Portland cement = 0.5; water = 30%; no added sodium silicate
p = waste/SPC = 0.75
q = waste/SPC = 0.50
r = waste/SPC = 0.25.

The results in Tables 13 and 14 were used to derive the suggested concrete recipes for each mixed waste under this study, which are summarized in Table 15. The basis for each of the recipes in Table 15 is 100 kg of mixed waste. It should be noted that each recipe took into consideration the amount of moisture contained in each untreated waste, as well as the waters of hydration that are present in the additive $Na_2SiO_3 \bullet 5H_2O$ (if used). In so doing, the amount of total water in a concrete mixture can be known with good accuracy, or a desired percentage of water can be achieved with excellent precision. The recipes in Table 15 should perform very well for the full-scale solidification of the indicated waste codes if the mixed waste sample material used in this study is representative of the remaining bulk of these mixed wastes, currently stored at the INEL.

One final comment should be made concerning the TCLP results presented herein. As Table 3 indicates, only a small fraction of the untreated mixed waste samples tested via TCLP actually contain hazardous amounts of toxic metals, as defined by RCRA. This result implies that many of the drums that currently reside at the Mixed Waste Storage Facility actually contain nonhazardous low-level waste instead of low-level mixed waste. In order to confirm which drums truly contain low-level mixed waste, drum-wise sampling should be performed, and those drums containing nonhazardous low-level waste could be slated for disposal at the INEL RWMC. In so doing, it may be possible to significantly decrease the number of drums in storage that are presumed to contain mixed waste.

Free Liquids Test Results

A free liquids test was performed on samples of the cured monoliths in accordance with EPA Method 9095, Paint Filter Liquids Test(21) and the results indicate that none of the concrete formulations used in this study produced monoliths that had free liquids. However, there were a small number of monoliths that had a thin layer of liquid on the top surface, which is common for hydraulic-type systems. Realistically, this liquid layer could be decanted and set aside for further treatment if it contains toxic amounts of heavy metals, then used as process or makeup water for other solidification work. It is worth noting that none of the formulations containing added sodium silicate contained such a liquid layer, as the sodium silicate appears to have effectively bound the excess water within the concrete matrices.

Radiological Screening of Monoliths

The monoliths that pass TCLP and free liquids tests are also required to satisfy radiation-related waste acceptance criteria (WAC) before they are disposed of into the RWMC at the INEL.

Generally, treated waste forms must undergo a gamma ray screening (at container surface and 3 ft (0.914m) from surface), and must not contain transuranic components or fissionable materials that are in quantities that exceed the limits imposed by the WAC. Since the WAC radiation limits are sensitive to the prevailing political climate (and hence may change from time to time), the specific numbers will not be given here. However, the reader is encouraged to consult the INEL manual that addresses WAC at the RWMC(22)> Finally, the waste material investigated herein was determined to be low-level waste prior to solidification, thus the alpha and beta activities of the treated mixed waste monoliths can be postulated from the radiological testing done to the untreated mixed waste samples.

Table 15. Suggested concrete recipes for LDR nonincinerable mixed waste (basis: 100 kg mixed waste).

INEL waste identification number	Dry Portland cement (kg)	Water[a] to add kg (wt% to water)	$Na_2Si0_3 \cdot 5H_20$ to add, kg (wt% Na_2Si0_3)	Water in raw waste, as used to derive recipe (wt%)
124 (solid)	167	73.0 (36)	0	49.4
128 (sludge)	200	31.6 (36)	0	87.8
128 (solid)	250	133.8 (30)	78.1 (8)	1.6
142 (solid)	200 kg SPC	NA	NA	NA (49.0)
153 (solid)	400 kg SPC	NA	NA	NA (10.5)
157(a) (liquid)	200	15.6 (36)	0	98.0
157(a) (solid)	167	100.8 (30)	59.4 (8)	2.2
186 (solid)	167	85.6 (30)	0	20.2
B&W (sludge)	200	7.1 (30)	0	85.0

a. The amount of water that is added depends on the desired percentage of water in the concrete recipe, the wt% water (moisture) in the raw waste, and the waters of hydration present in the added $Na_2Si0_3 \cdot 5H_20$.

NA — not applicable.

NOTE: Waste codes 142 and 153 were solidified with SPC.

CONCLUSIONS AND RECOMMENDATIONS

This report has provided a summary description and evaluation of Portland cement-based and SPC-based solidification of mixed wastes generated at the INEL, as performed under a bench-scale RCRA treatability study. The basis of this evaluation is the ability of a given monolith recipe to satisfy pertinent disposal criteria, namely, TCLP and free liquids tests.

The results indicate that Portland cement systems can be used to successfully immobilize toxic metals in solid, liquid, and sludge mixed waste material. Of the 92 hydraulic monoliths produced under the experimental design matrix, only three failed TCLP criteria for the toxic metals of concern. Only three SPC-based monoliths failed TCLP. Concerning free liquids tests, no monoliths possessed free liquids as defined by EPA Method 9095 (Paint Filter Liquids Test) (23).

The data presented herein indicate that the most favorable concrete formulations are waste-specific, but overall have the following general composition: the ratio of waste to dry Portland cement is 0.5 to 0.6, with 30–36 wt% water. This composition range takes into consideration the need to incorporate as much waste as possible into the monolithic form, thereby minimizing the solidified volume produced per unit of treated

waste, while satisfying the waste disposal criteria for TCLP (RCRA metals) and free liquids. Such results infer that it may be possible to load the concrete with even greater amounts of waste while satisfying disposal criteria(24).

The addition of Na_2SiO_3 appears to be optional for most of the concrete formulations, considering the disposal criteria of passing TCLP and free liquids tests. This additive should be used only with good cause, as its use will result in greater treatment costs and greater disposal costs due to the small increase of the monolithic mass and volume that it causes. Finally, sodium silicate should not be added to concrete mixtures that contain INEL waste code 186, as it appears to promote the leaching of cadmium from this treated waste.

INEL waste code 142 appears to be better suited for Portland cement systems than SPC. This is largely due to the moisture content of this waste (roughly 50% water), which makes it more compatible with hydraulic-based systems. If solidified with Portland cement, this mixed waste would require no pretreatment aside from mixing and blending. Also, when INEL waste code 142 is dried, it has a relatively low density (about 0.4 g/cc), which tends to make it float to the top of molten SPC. This floating problem could be eliminated by using a Portland cement system with a higher viscosity than molten SPC.

INEL waste code 153, as sampled, contained a small amount of elemental mercury that apparently caused the solidified monoliths for this waste to exceed the RCRA limit for mercury. Regardless of the full-scale solidification technique that will be used on this mixed waste, a pretreatment step should be used wherein the elemental mercury is effectively removed from the waste matrix. A gravity-based separation technique would be a good candidate for such a pretreatment step.

Finally, this study is valuable in that it demonstrates which concrete recipes succeed in passing disposal criteria, and which ones fail. The recipes that fail serve to define a set of limiting conditions (here, the concrete formulation) that can be used as a baseline for future solidification of a particular waste. Monoliths can fail TCLP or free liquids tests because of one or more reasons: (a) the untreated waste form could be unprepared for solidification (e.g., a soil that has elemental mercury), (b) the untreated waste form could be incompatible with the solidification technique, or (c) improper mixing or an errant recipe could produce a monolith that is chemically or mechanically unstable. A monolith recipe that fails one or more disposal criteria should be investigated further. For this study, treated samples of INEL waste codes 153 and 186 failed TCLP tests, along with the HGSOIL waste (Appendix B). These wastes should undergo further bench-scale studies until optimal recipes are derived. Even though there are suggested recipes given in Table 15 for waste codes 153 and 186, these recipes may not be optimal, as they were the recipes determined by the particular experimental design matrix used for this treatability study. A different design matrix could produce optimal recipes that differ slightly from what are given herein.

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Appendix A

SPC Handling Procedures

Process Steps (as done for bench-scale solidification):

1. Gently heat moist waste to complete dryness, preferably overnight in an oven or on a hot plate.

2. Place the SPC into the melting pot; adjust the thermostat to achieve approximately 280–290°F (138-143°C), which should be monitored via a thermometer positioned in the molten SPC.

3. Into each monolith cast, weigh in a predetermined amount of dry waste.

4. Preheat monolith cast and contents to 280–290°F.

5. Once the SPC has melted and the temperature has become steady, transfer/weigh a given amount of SPC into a pre-heated monolith cast, which should be on a heat-resistant pad on the balance. It may be advantageous for mixing if only a portion of the prescribed waste is present in the monolith cast when the SPC is poured in.

6. Stir and mix contents for two to four minutes, stirring in any remaining pre-heated mixed waste material.

7. Pour in a thin SPC "cap" as a final seal if needed.

8. Set monoliths aside for hardening and cooling; label as needed.

Health and Safety Concerns:

1. All work should be done inside a negative pressure ventilation hood.

2. A H_2S and/or SO_2 monitor should be placed near the person doing the handling of the molten SPC.

3. Heat-resistant clothing should be used where needed. Heat-resistant gloves are recommended.

4. Avoid direct handling of heated surfaces. Use tools (e.g., tongs) to minimize the risk of burns.

5. Molten SPC should not be poured over "wet" waste, as the steam generated may initiate chemical reactions or cause spattering of the waste. Also, avoid mixing SPC with strong oxidizers, such as nitrate salts.

Appendix B

Additional Solidification Not Included in Experimental Design Matrix

In addition to the mixed wastes investigated through the experimental design matrix of this bench scale study, there are other mixed or hazardous wastes that could be treated by solidification with Portland cement.[B-1] These include EDTA-laden liquid wastes, IET valve pit waste, File 8 sludges, plating solution wastes, many wastes currently residing at the Mixed Waste Storage Facility (MWSF), and any other waste that would exhibit favorable compatibility with Portland cement.

Some of these one-of-a-kind wastes were investigated by this study, where Portland cement and SPC were used to solidify small samples of this low-level MW material, which included rinsing and paper towel wastes from the bench-scale solidification experiments, IET Valve Pit waste liquid, File 8 waste sludge, and mercury-contaminated sludge leftover from an amalgamation study.[B-2] The same solidification methodology was used on these MW samples as was used on the waste samples discussed in the main body of this report. The solidification results for these additional mixed wastes are discussed and summarized below.

Monolith ID: RINSE.SL.HCA1
Waste Source: Rinsing waste accumulated during bench-scale solidification study.
Solidification Method: Portland cement with added sodium silicate.
TCLP Before Solidification: Not Done.
TCLP After Solidification: 190 μg/L Hg (average from duplicate analyses: 282 and 98 μg/L).

Monolith ID: RAGS.SPC1, RAGS.SPC2
Waste Source: Paper towel and SPC waste accumulated during bench-scale solidification study.
Solidification Method: SPC.
TCLP Before Solidification: Not Done.
TCLP After Solidification: RAGS.SPC1: 78 μg/L Pb (DL), 0.1 μg/L Hg (DL)
RAGS.SPC2: 78 μg/L Pb (DL), 0.4 μg/L Hg.

Monolith ID: IETVP.L.HCA1
Waste Source: IET Valve Pit liquid waste.
Solidification Method: pH adjustment; Portland cement with added sodium silicate.
ICP[B-3] Before Solidification: 16,000 to 18,000 μg/L Pb, 800 to 1,500 μg/L Hg.
TCLP After Solidification: 78 μg/L Pb (DL), 0.1 μg/L Hg (DL).

B-1. D. R. Haefner, "Proposed Treatments of Liquid Wastes from the MWSF", EG&G Idaho, Engineering Design File Serial No. WROC-EDF-146, October 1992.

B-2. D. R. Tyson, Treatability Study for the Amalgamation of a Radioactively Contaminated Elemental Mercury Waste at the Idaho National Engineering Laboratory, EG&G Idaho, Document No. EGG-WMO-10392, October 1992.

B-3. ICP = Induced Coupled Plasma Analysis; performed at the INEL.
DL = Detection Limit.

Monolith ID: FILE8.SL.HCA1
Waste Source: File 8 sludge waste.
Solidification Method: Portland cement with added sodium silicate.
TCLP Before Solidification: 910,000 μg/L Pb, 128 μg/L Hg.
TCLP After Solidification: 146 μg/L Pb, 0.31 μg/L Hg.

Monolith ID: HGSOIL.SL.HC1, HGSOIL.SL.HC2, HGSOIL.SL.HCA1, HGSOIL.SL.HCA2
Waste Source: mercury-contaminated soil/sludge leftover from an amalgamation study.[B-2]
Solidification Method: Precipitation, then Portland cement with and without added sodium silicate.
TCLP Before Solidification: Not Done.
TCLP After Solidification: HGSOIL.SL.HC1: 29,300 μg/L Hg
HGSOIL.SL.HC2: 11,200 μg/L Hg
HGSOIL.SL.HCA1: 17,100 μg/L Hg
HGSOIL.SL.HCA2: 18,100 μg/L Hg

It is seen that all of the above monoliths passed TCLP for the toxic metals of concern, except the monoliths that are part of the "HGSOIL" group. The untreated waste used for the HGSOIL monoliths was a diverse, sludge-like mixture of soil, organic matter (twigs, leaves, etc.), water, and elemental mercury. An initial attempt had been made to acidify the elemental mercury in this material to transform the mercury into the ionic form which could then be chemically precipitated. However, a small amount of elemental mercury still remained in the acidified mixture, which is suspected to have caused the HGSOIL monoliths to exceed RCRA limits for mercury. If similar waste forms are encountered in the future, a pretreatment scheme should be developed that would remove most of the elemental mercury. Perhaps a gravity-based separation would be ideally suited for such a scenario.

MIXED WASTE SOLIDIFICATION TESTING ON THERMOSETTING POLYMER AND CEMENT BASED WASTE FORMS IN SUPPORT OF HANFORD'S WRAP MODULE 2A FACILITY

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ABSTRACT. A testing program has been conducted by the Westinghouse Hanford Company to confirm the baseline waste form selection for use in Waste Receiving and Processing (WRAP) Module 2A. WRAP Module 2A will provide treatment required to properly dispose of containerized contact-handled, mixed low-level waste at the U.S. Department of Energy Hanford Site in south-central Washington State. Solidification/stabilization has been chosen as the appropriate treatment for this waste. This work is intended to test cement-based and thermosetting polymer solidification media to confirm the baseline technologies selected for WRAP Module 2A.

Screening tests were performed using the major chemical constituent of each waste type to measure the gross compatibility with the immobilization media and to determine formulations for more detailed testing. Surrogate wastes representing each of the eight waste types were prepared for testing. Surrogates for polymer testing were sent to a vendor commissioned for that portion of the test work. Surrogates for the grout testing were used in the Westinghouse Hanford Company laboratory responsible for the grout performance testing. Detailed discussion of the laboratory work and results are contained in this report.

INTRODUCTION

A testing program has been conducted by Westinghouse Hanford Company (WHC) to confirm the baseline waste form selection for use in Waste Receiving and Processing (WRAP) Module 2A. WRAP Module 2A will provide treatment required to properly dispose of contact-handled (CH), mixed low-level waste (MLLW) accumulating at the U.S. Department of Energy (DOE) Hanford Site in south-central Washington State. Solidification/stabilization has been chosen as the appropriate treatment for this waste.

The testing used a phased approach consisting of first screening the compatibility of surrogate wastes with the immobilization media and then performing detailed physical and chemical tests on laboratory-prepared surrogate waste forms. This will be followed by testing of surrogate waste form specimens prepared by full-scale mixing equipment.

The focus of this first phase of test work is to verify the ability of the conceptual design identified immobilization media to adequately solidify those waste types proposed as feed to WRAP Module 2A (1). Two matrices for waste solidification have been selected: cement-based materials and thermosetting polymer resins. Eight different waste types were used for these initial phases of testing. Four of the waste types were tested with grout waste forms, and four waste types were tested with the thermosetting polymer. Test criteria for solidified mixed waste were assembled from applicable regulatory documentation (2-4), including guidance documents from the U.S. N R C (5) and E P A (6).

Screening tests were performed using the major chemical constituent of each waste type to measure the gross compatibility with the immobilization media. The results of these tests were positive and are discussed later in the report.

Surrogate wastes were then prepared by WHC to represent each of the eight waste types for testing. Surrogates for polymer testing were sent to a vendor commissioned for that portion of the test work. Surrogates for the grout testing were used in the WHC laboratory responsible for the grout performance testing. Solidified test specimens were prepared for both the grout and polymer waste forms with the surrogate wastes, and tests were performed. Detailed discussion of the laboratory work and results are contained in this report. All grout specimens performed as expected and confirmed baseline process selection. Test results from the polymer demonstrated that an adequate product could be made that passed all acceptance criteria. Some negative results were encountered on the leachability of some hazardous constituents (chrome at high waste loadings and mercury). The polymer tests also indicated that leaching results for hazardous constituents, as tested by the toxic characteristic leach procedure (TCLP) method, are dependant on the sample preparation method.

WASTE TYPES DESCRIPTION AND WASTE FORM SELECTION

A general description of the feedstreams chosen for this test work follows.

Liquid Effluent Treatment Facility Secondary Solids

Two liquid effluent treatment facilities are planned for construction at the Hanford Site. The C-018 Facility and the L-045 Facility will produce several secondary waste streams that may be both radiologically and chemically hazardous. The two major waste streams from these facilities include:

- Ammonium Sulfate. The major secondary waste from the C-018 process will be an ammonium sulfate cake produced in an evaporative crystallization process using a thin film evaporator. The high ammonia content of the treatment waste water and the addition of sulfuric acid in the C-018 process led to the formation of ammonium sulfate. This waste stream will be generally greater than 90 wt% ammonium sulfate with trace regulated contaminants such as chromium and mercury. The waste will be dried before shipment out of the C-018 Facility.
- Metal Sludge. The L-045 Facility will use a co-precipitation process to remove dissolved contaminants. An iron hydroxide is the baseline precipitation agent in the process. The precipitates are assumed to include various soluble metal contaminants that will be regulated. The sludge will be filtered and possibly dried before shipment from the L-045 Facility.

183H Solar Basin Waste

The 183H Solar Evaporation Basins were used to reduce waste by natural evaporation of liquid chemical wastes generated as part of reactor fuel fabrication activities. The liquid waste discharged to the four concrete basins consisted primarily of spent acid etch solutions (sulfuric, nitric, hydrofluoric, and chromic acids). This waste was generally neutralized with sodium hydroxide before discharge to the basins. The wastes contained various metallic contaminants. Several types of nonroutine wastes were also discharged to the basins. The basins eventually ceased accepting waste and subsequently were found to have failed and leaked. A timely cleanup and closure of the basins was then pursued. The following waste streams from this cleanup were included in this testing program.

- 183H Crystalline Solid. The evaporation of the liquid waste also produced a crystalline solid consisting mostly of salts of nitrate, sulfate, fluoride, and sodium. These wastes were removed from the basins and packaged in poly-lined 208-L (55-gal) drums without further treatment.

- 183H Sludge. The remaining fraction of waste in the 183H Basins was a sludge-like material consisting of a mixture of mostly sodium sulfate and sodium nitrate. This fraction was also relatively high in copper content and had more apparent water content than the other wastes (thus its sludge-like consistency). The sludge was packaged in drums with an absorbent material, but had no further treatment.
- 183H Miscellaneous Cleanup. After removal of the waste from the basins, contamination remained on the concrete floors and walls. These areas were sandblasted to remove this contamination, resulting in another waste form. Also, cleanup of tumbleweeds and various tools and structures used in the operation were packaged as additional waste.

Ash From Thermal Treatment

This waste will be produced by the proposed thermal treatment facility for organic mixed waste. The ash residue from this process may need to be treated to account for residual contamination in the waste or to meet treatment standards for mixtures of waste types. Table 1 shows the specific waste types and selected waste forms.

Table 1. Treatability testing waste types and waste forms.

Test ID	Title	Cement Based Testing	Polymer Testing
Type 1	C-018 Ammonium Sulfate	Yes*	Yes
Type 2	183H Sludge (Basins #1 and #2)		Yes
Type 3	183H Sludge (Basins #3 and #4)		Yes
Type 4	183H Crystalline Solid		Yes
Type 5	183H Misc. Clean-up (High Cu)	Yes	
Type 6	183H Misc. Clean-up (High NO_3)	Yes	
Type 7	L-045 Metal Sludge	Yes	
Type 8	Ash from Thermal Treatment	Yes	

*Envirostone - A trademark of the American Gypsum Company.

Table 1 shows that several of the feedstreams were split into numerous waste types for testing to group wastes with similar chemical constituents. The first four waste types were chosen for testing with the thermosetting polymer because of their high soluble salt content (including high nitrate content), which is known to cause problems with cement solidification. Waste types 5 through 8 were chosen for testing with cement waste forms because they do not contain a high content of any constituents that interfere with cement solidification. Type 1 waste demonstrates a special problem with cement; that is, the ammonium sulfate would react with the high pH solutions in ordinary portland cement, evolving ammonia gas. Envirostone*, a gypsum-based cement that exhibits a neutral pH, was selected as an alternative to ordinary portland cement for this waste stream.

Surrogate formulas for each of the eight feedstreams were developed and then prepared in the WHC laboratories. Table 2 shows approximate compositions for the surrogates.

Table 2. Surrogate wastes approximate composition.

Component	Waste Type 1 LETF Salts	Waste Type 2 Basins #1, #2 Sludge	Waste Type 3 Basins #3, #4 Sludge	Waste Type 4 Basin Crystal Solids
Silver (ppm)		218	190	
Barium (ppm)			24	100
Beryllium(ppm)		6	2.3	
Cadmium (ppm)			6	
Chromium (ppm)	187.5	900	390	500
Copper (ppm)	201.0	130,000	112,000	63,000
Mercury (ppm)	9.2	1.3		
Nickel (ppm)	46.5	100	130	400
Subtotal (ppm)	444.20	131,225.30	112,742.30	64,000.00
Ammonium (%)	22.83			
Fluoride (%)		6.0	1.3	7.1
Nitrate (%)	1.1	13.5	26	1.6
Sodium (%)		20.0	24	22.9
Sulfate (%)	64.61	20.2	3.7	35.5
Water (%)	10.0	21.58	25.03	24.5
Subtotal (%)	98.54	81.28	80.03	91.60
Inerts (%)	1.42	5.6	8.7	2.0
Total (%)	100.00	100.00	100.00	100.00

Waste Surrogates for Cement Testing:
Type 5 - 90% Sandblast Grit w/10% Type 2 similar contamination.*
Type 6 - 90% Sandblast Grit w/10% Type 4 similar contamination.*
Type 7 - 98.7% Ferric Oxide Reagent, 1.3% Sodium Sulfide, 0.7% Polymer Flock.*
Type 8 - 90% Fly Ash, 8% Clay, 2% Sand.*

*Trace contaminants and concentrations used for cement testing surrogates are detailed later in the report on the table reporting results for solidified product leach testing.

Test Selection and Acceptance Criteria

The main objective of the waste treatability testing is to demonstrate the successful treatment of CH-LLMW feed streams using the technologies proposed for use in WRAP Module 2A. To demonstrate successful treatment, the final waste forms must be subjected to numerous tests to show compliance with all applicable regulatory requirements. Table 3 summarizes the tests that were performed and the performance acceptance criteria. The tests were selected to cover a broad spectrum criteria that could be imposed on the final waste form. The acceptance criteria are composed of a conservative set of tests and requirements that were compiled from several sources including the U.S. Nuclear Regulatory Commission, U.S. Environmental Protection Agency, Washington State Department of Ecology, and Hanford Site specific solid waste acceptance criteria (7).

Table 3. WRAP Module 2A waste form performance specifications.

Waste Form Characteristic	Test Method	Acceptance Criteria
Compressive Strength	ASTM D695 or ASTM C39	Strength > 500 psi
Leachability Index	ANS 16.1	Leach Index > 6
Biodegradation	ASTM G21 and G22, ASTM D695 or ASTM C39	No growth, Strength > 500 psi
Thermal Cycling	ASTM B553, ASTM D695 or ASTM C39	Strength > 500 psi after 30 thermal cycles
Radiation Stability	ASTM D695 or ASTM C39	Strength > 500 psi after irradiation to 10^8 rad
Immersion	ASTM D695 or ASTM C39	Strength > 500 psi after 90-day water immersion
Free Liquids	ANS 55.1	Free liquid < 0.5%
Hazardous Characteristics	40 CFR 261	Not ignitible, not corrosive, not reactive
Toxicity Characteristics	EPA 1311 (TCLP), EPA 6010	TCLP leachable constituents below EPA limits*

NOTE: Multiply psi by 0.07031 to obtain kg/cm^2.
*EPA limits as described in 40 CFR 268.41, Table CCWE.
ASTM = American Society for Testing and Materials
ANS = American Nuclear Society
EPA = U.S. Environmental Protection Agency.

Testing Description and Results

The waste treatability test work for WRAP Module 2A is using a phased approach. Test work can be broken down into three phases:

Phase 1. Screening Tests - Screening of waste form compatibility with waste types
Phase 2. Surrogate Performance Testing - Detailed testing of waste forms produced on a laboratory scale with surrogate waste
Phase 3. Full-scale and advanced laboratory studies aimed at developing chemical and physical operating parameters for the selected processes, which is not covered by this report.

Phase 1: Screening Tests - Cement-Based Waste Forms. The cement-based waste form screening was performed in WHC laboratories to test the raw compatibility of the waste chemicals with cement and to narrow in on the best type of cement formulation, given a specific waste type. Several types of cements and various formulations (waste loadings) were used with each waste type, and setting characteristics were observed. Table 4 lists the selected cement formulations based on these screening tests.

Some special complications were discovered through the fast set characteristics exhibited by the Envirostone when mixed with an ammonium sulfate (Type 1). The set occurred too rapidly to be of use in a typical

mechanical mixer. A slow set Envirostone was tried with little or no success; however, the use of citric acid or sodium citrate retarders were successful.

Table 4. Cement binder formulations from screening tests.

	Type 1	Type 5	Type 6	Type 7	Type 8
Waste	Ammonium sulfate 11.5 wt%	Grit/Sludge 41.7 wt%	Grit/Solids 41.7 wt%	Ferric oxide 15.4 wt%	Ash mix 30.0 wt%
Primary binding agent	Envirostone 57.5 wt%	Type III 41.6 wt%	Slag cement 37.5 wt%	Type III 42.6 wt%	Slag cement 40.5 wt%
Additive 1	Citric acid 1.1 wt%	-	Type III 4.2 wt%	-	Type III 4.5 wt%
Additive 2	Sodium bicarb. 1.1 wt%	-	-	-	-
Water	28.7 wt%	16.7 wt%	16.7 wt%	38.5%	25 wt%

Phase 1: Screening Tests - Thermosetting Polymer Waste Form. Screening tests for the thermosetting polymer immobilization process were performed at a private vendor's (Diversified Technologies) rented laboratory space at Saginaw Valley State University. Fifteen screening tests were performed using Diversified Technologies vinyl ester polymer immobilization process. The technique was observed by the attenders and videotaped by WHC. The materials that were solidified were intended to represent the major chemical characteristics of the wastes selected for thermosetting polymer testing and some waste samples that the vendor had prepared for demonstration. The materials that were solidified included reagent grade sodium nitrate, ammonium sulfate, and hydrated sodium sulfate (major chemical constituents of waste being treated with polymer). The chemicals were used in both wet and dry form and in combination with diatomaceous earth to simulate both crystalline and sludge-type material.

All specimens gelled within a short period of time (~1 to 10 mins.) and reached full strength and hardness within 30 mins. The process successfully immobilized sodium nitrate and ammonium sulfate at 60 wt% loading with no apparent side reactions. The samples that contained hydrated sodium sulfate crystals exuded some free liquid during the curing exotherm of the polymer (as much as 2 wt%). This occurred both with wet and dry waste loadings.

Formulation development tests were then performed by Stock Equipment Company to obtain a qualitative measure of waste loading capacity, chemical compatibility, and free water generation. The initial trials were successful for Type 1 and Type 3 surrogates. Additional investigation of Type 2 waste revealed that the pH of the surrogate did not resemble the actual waste. The pH of Type 2 surrogate was adjusted to 10.5 to more closely resemble the actual waste, and a suitable formulation was developed for Type 2 and 4 waste using a different binder material. Table 5 summarizes the formulations that were used to prepare the waste form specimens.

Phase 2: Surrogate Performance Tests - Cement-Based Waste Form Results. The cementitious waste forms were prepared by combining the waste surrogates and the cementitious binders according to the formulations developed during the screening tests. The surrogate material and the cementitious binder were measured into a 18.9 L (5-gal) capacity, heavy duty Hobart variable mixer, where they were mixed until a homogeneous mixture was obtained. A minimum of 9.5 L (2.5 gal) of cement-waste slurry was required for each set of experiments. For each waste type tested, a cement-waste slurry was prepared in three batches and poured out separately into the appropriate sized molds. Sample molds included 5-cm by 5 -cm

(2-in. by 2-in.) cubes, small cylinders of 7.6 cm (3 in.) diameter by 15.2 cm (6 in.) high, and large cylinders of 15.2 cm (6 in.) diameter by 30.5 cm (12 in.) high. The wet specimens were covered with plastic or placed in plastic bags to simulate placement in a 208-L (55-gal) drum or another sealed container. The cube samples were removed from their metal molds after approximately 3 days. The samples were labeled and placed in plastic bags at room temperature until the appropriate cure time was achieved. After curing, the samples were weighed and then tested. The cylinders were kept in their molds and covered until tested. Cement controls (no waste) were made for compression strength reference. Tables 6 and 7 describes the results of the tests.

Table 5. Polymer formulation parameters.

Formulation Parameter	Type 1	Type 2	Type 3	Type 4
Waste/Binder ratio, Kg/Kg	4/2	3/3	4/2	3/2
Binder type	A*	B*	A*	B*
Catalyst dose, wt% of binder	2.5	7.5	2.5	5.0
Promoter dose, wt% of binder	0.1	2.0	0.1	1.0
Total mixing time, minutes	25	8.5	8.5	10.5
Peak mixing power, watts	45	12.3	9.9	13.9
Peak exotherm, degrees C	38.2	70	57.5	63
Peak exotherm time, minutes	75	30	120	25

*Note: The use of "A" and "B" denotes that two different binders were used for this test work to accommodate the waste types.

Table 6. Cement-based waste form results.

Waste Type	Compressive Strength* (psi)	Radiation Stability	Biodegradation	Leach Index	Water Immersion 14/42/90 days	Thermal Cycle
Control	7400/4500	-	-	-	-	-
5	7100/5400	8500/9100	10300	12.2 (Ru)	8900/3900/ 8400	5500/8000
6	3500/4200	3800/4800	6100	12.7 (Co)	5300/2600/ 5500	4000/4400
7	2800/2100	2500/2000	3100	9.7 (Na)	2400/1100/ 3000	2200/2400
8	3400/2400	4100/3900	4600	12.7 (Ru)	3900/2500/ 4380	2900/3100
1	<50/70	35/<50	>50	9.9 (Ce)	failed	>50/50

NOTE: Multiply psi by 0.07031 to obtain kg/cm^2.
*Compressive Strength reported for small cylinder/large cylinder per ASTM Standards specified in Performance Specifications - large cylinder specific to cement forms.

The results indicate that the formulations developed in Phase I were successful at immobilizing each of the waste types, with the exception of the ammonium-sulfate waste. The waste forms produced from waste types 5, 6, 7, and 8 contained no free water, exhibited compressive strengths well above what is required, and passed the TCLP tests. These waste types will be further evaluated for grout processing in WRAP Module 2A.

Table 7. TCLP results for WRAP Module 2A cement waste forms.

Waste Type	Species	Orig. Cont.	TCLP Cont.	Limit	Pass/Fail
5	Chromium	50 ppm	0.07 ppm	5 ppm	Pass
	Copper	1.7%	0.09 ppm	No limit	N/A
6	Chromium	50 ppm	<0.02 ppm	5 ppm	Pass
7	Chromium	100 ppm	<0.03 ppm	5.0 ppm	Pass
	Mercury	100 ppm	<0.1 ppb	0.2 ppm	Pass
8	Barium	100 ppm	0.05 ppm	100 ppm	Pass
	Cadmium	100 ppm	<0.01 ppm	1.0 ppm	Pass
	Chromium	500 ppm	0.3 ppm	5.0 ppm	Pass
	Lead	100 ppm	<0.12 ppm	5.0 ppm	Pass
	Mercury	100 ppm	0.5 ppb	0.2 ppm	Pass
	Selenium	100 ppm	<0.12 ppm	1.0 ppm	Pass
	Silver	100 ppm	<0.02 ppm	5.0 ppm	Pass
1	Chromium	700 ppm	4.0 ppm	5.0 ppm	Pass
	Mercury	10 ppm	0.3 ppb	0.2 ppm	Pass
	Nickel	50 ppm	0.25 ppm	No limit	Pass

Phase 2: Surrogate Performance Testing - Thermosetting Polymer Waste Form. Polymer waste forms testing was performed at vendor facilities (Stock Equipment Company). Solidified test specimens were prepared from waste surrogates in a batch size of approximately 4.7 L (1.25 gal). A variable speed lab mixer with propeller blades operating at 1800 rpm was used. Each set of specimens was made from a single batch and poured into cylindrical molds. The tests described above were performed on the specimens. Replicate tests were also performed.

Table 8 summarizes results of the testing. All specimens were successfully immobilized and exhibited strength and durability characteristics meeting or exceeding the waste form performance specifications. Type 3 surrogate met all of the performance specifications. Leaching characteristics for all surrogates met the requirements for low-level waste, but some TCLP constituents of types 1, 2, and 4 surrogates exceeded the allowable limits.

The TCLP results prompted additional work to develop formulations that could meet the regulatory limits for chromium and mercury. Additional testing was performed using waste loading of 25 wt%. Three methods for preparing the TCLP extraction specimens were investigated. One method involved casting pellets from the mixture so no size reduction was required. The other two methods used larger specimens, which were crushed to meet the size requirements for TCLP; all material was extracted for one method, and the other method discarded fines less than 1-mm screen size prior to extraction.
Both crushing methods were unable to meet TCLP limits for mercury. The pellet method passed for all TCLP constituents present. The use of reduced waste loadings was successful in decreasing the concentrations of TCLP metals observed in the waste extracts, but the sample preparation method apparently

has a larger influence on the final results than waste loading. Further investigation is planned to address these concerns.

Table 8. Summary of polymer waste form testing results.

Waste Form Characteristic	Acceptance Criteria		Test Results			
			Type 1	Type 2	Type 3	Type 4
Compressive Strength	Strength > 500 psi		2472 psi	1085 psi	1411 psi	942 psi
Leachability Index	Leach Index > 6 Demin/Sea water	Cs	7.7/7.4	7.0/7.0	7.3/7.2	7.1/7.1
		Co	8.2/7.9	9.2/9.3	10.1/10.3	7.5/7.7
		Sr	8.9/8.7	9.3/9.1	10.2/9.4	9.1/9.0
Biodegradation	No growth, Strength > 500 psi		No Growth	No Growth	No Growth	No Growth
			2247 psi	3710 psi	994 psi	1114 psi
Thermal Cycling	Strength > 500 psi after 30 thermal cycles		5111 psi	640 psi	990 psi	850 psi
Radiation Stability	Strength > 500 psi after irradiation to 10^8 rad		5127 psi	6028 psi	964 psi	2575 psi
Immersion	Strength > 500 psi after 90-day immersion		1114 psi/ 1151 psi	1034 psi/ 842 psi	1048 psi/ 952 psi	981 psi/ 1028 psi
Free Liquids	Free liquid < 0.5%		Pass	Pass	Pass	Pass
Hazardous Characteristics	Not ignitible, not corrosive, not reactive		Pass Pass Pass	Pass Pass Pass	Pass Pass Pass	Pass Pass Pass
Toxicity Characteristics	TCLP leachable metals below EPA limits (parts per million)	Ba 100	N/A*	N/A	0.511 pass	0.183 pass
		Cd 1.0	N/A	N/A	0.270 pass	N/A
		Cr 5.0	2.43 pass	9.61 fail	4.65 pass	8.88 fail
		Hg 0.2	1.65 fail	1.54 fail	N/A	N/A
		Ag 5.0	N/A	0.355 pass	0.397 pass	N/A

NOTE: Multiply psi by 0.07031 to obtain kg/cm^2.
*N/A = Not applicable.

CONCLUSIONS

The immobilization/stabilization technologies selected for use in WRAP Module 2A have been tested on waste surrogates reflecting the chemical characteristics of 80% of the baseline feed volume. The baseline process selection has been confirmed for the feed streams studied. Suitable formulations have been developed and waste form performance testing has shown that the technologies are capable of meeting all applicable regulatory acceptance criteria.

Cementitious grout formulas based on type I and type III portland cement, type S slag cement, or blends of these materials have been developed for four baseline waste streams. Performance test results met or

exceeded all waste form performance specifications. Attempts to develop a gypsum-based formulation for the ammonium sulfate waste surrogate were unsuccessful.

Thermosetting polymer formulations have been developed for four additional baseline waste streams. Waste surrogates were successfully immobilized at waste loadings from 50 wt% to 66 wt%. Performance test results met all specifications except TCLP for chromium and mercury. Specimens prepared with a 25 wt% waste loading met TCLP limits for all constituents. TCLP results for polymer waste forms were shown to be highly dependent on the method used for TCLP sample preparation.

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CHAPTER 2

Alternative Treatment Technologies

PRIVATE SECTOR PARTICIPATION FOR THE TREATMENT OF DOE AND COMMERCIAL RADIOACTIVE MIXED WASTES

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ABSTRACT. The ability of the U.S. Department of Energy (DOE) to accept commercial low-level mixed waste (LLMW) for disposal has been identified as a technically feasible alternative in developing a strategy for managing commercial mixed waste. This document is an estimation of DOE's capabilities to assist the state compacts and the commercial sector with the difficult issues related to the treatment and disposal of LLMW. The first step in determining DOE's capabilities to assist the commercial sector and the state compacts in managing their LLMW is to establish how closely DOE's LLMW resembles the LLMW generated commercially. This report established that a large portion of the low-level mixed waste streams are common to both the DOE and private sectors. A united approach between the DOE and the host states and compacts to cooperatively manage the low-level mixed wastes (LLMW) would prove to be beneficial to all.

INTRODUCTION

In today's environmentally conscious political arena, the controversial issues of low-level mixed waste (LLMW) disposal have required the states to take active roles in developing strategies for managing commercially generated wastes. The Low-Level Radioactive Waste Amendments Act of 1980 authorized the establishment of compacts by two or more states for the safe and efficient management of low-level radioactive wastes. The Low-Level Radioactive Waste Policy Amendments Act, enacted on January 15, 1986, assigned individual states or compact regions the responsibility for disposing of low-level radioactive wastes (LLRWs), including commercial mixed wastes, generated within those states or compacts after December 31, 1992.

In accordance with the mixed waste guidance (1) published by the U.S. Environmental Protection Agency (EPA) in 51 Federal Register 24,505 (July 3, 1986) low-level radioactive wastes containing radioactive materials regulated under the Atomic Energy Act (AEA) and hazardous wastes regulated under Subtitle C of the Resource Conservation and Recovery Act (RCRA) are subject to both sets of statutory requirements. In particular, commercial "mixed wastes" must meet the treatment standards as specified in 40 CFR part 268 (2) and the waste form requirements set forth in 10 CFR part 61 (3) prior to land disposal in a unit meeting both RCRA and AEA standards. This duality in treatment requirements is reflected in technology development initiatives. Significant technology development has been conducted for either radioactive or hazardous waste, but limited technology development, specifically addressing mixed waste treatment issues, has been completed. Final waste form criteria have not been established for all types of treatment residues. Technology has not been designed, developed, demonstrated, or tested to produce a low-risk final waste form.

Mixed waste is a problem because the definitive treatment standards and the capacity to treat have not been established and few disposal facilities are available. Therefore, sites currently generating mixed waste are storing these wastes for future disposal, despite the fact that the Land Disposal Restrictions (LDR) contained within RCRA mandates schedules for treatment regardless of whether treatment standards or applicable treatment technologies exist. With regard to treatment and disposal of mixed waste, many generators may be operating out of compliance.

The low waste volumes generated by commercial facilities, the high regulatory burdens, the public opposition to new disposal sites, and the relatively high cost of constructing proper disposal facilities combine to make alternative strategies for the management of mixed waste more attractive. In response, the Low-Level Waste Forum, an organization comprised of States with proposed or operating low-level waste disposal sites requested in October 1990 that "the U.S. Department of Energy (DOE) explore an agreement with host states and compacts under which DOE would accept commercial mixed low-level radioactive waste at DOE's own treatment and disposal facilities." (4)

A united approach between the DOE and the host states and compacts to solve the treatment, storage, and disposal issues associated with LLMW would prove to be beneficial to all. There is a clear need for technologies designed to meet the unique requirements for mixed waste processing and for a system-wide integrated strategy to develop treatment technology and deploy the capability to treat mixed waste.

One of the first steps in determining DOE's capabilities to assist the commercial sector and the state compacts in managing their LLMW is to establish how closely DOE's LLMW resembles the LLMW generated commercially. A total of approximately 179,000 m^3 of mixed waste is being stored at DOE sites located throughout the United States. In addition, the generation of mixed waste continues at an approximate rate of 81,000 m^3/year. The commercial sector mixed waste volume is very small in comparison to the DOE's waste streams. Currently, it is estimated that 1,339 m^3 of commercially generated mixed waste was stored as of December 31, 1990 with an additional 3,864 m^3/year being generated.

Source of Commercial Sector Mixed Waste Information

All information regarding commercially generated LLMW was obtained from the joint U.S. Nuclear Regulatory Commission (NRC) and EPA sponsored project entitled National Profile on Commercially Generated Low-Level Radioactive Mixed Waste preformed by Oak Ridge National Laboratory (ORNL). The overall objective of this project was to compile a national profile on the volumes, characteristics, and treatabilities of commercially generated mixed waste for five major facility categories -- academic, industrial, medical, NRC-licensed government facilities, and nuclear utilities. Findings of the above mentioned project were incorporated into a report entitled "National Profile on Commercially Generated Low-Level Radioactive Mixed Waste." (2) (This report will be referred to here after as the National Profile).

The National Profile is a statistically based estimation of the 1990 generation rates and volume of commercially generated mixed waste in the five facility categories mentioned above. The amount of mixed waste generated in 1990 and in storage as of December 31, 1990 was estimated by considering the responses of 1,323 questionnaires which were sent to a broad spectrum of potential generators of mixed waste within the five facility categories. The survey target population included a total population of 2,936 facilities. The survey responses of 1,016 facilities (77% response rate) were place into nine databases created to sort and manage all information collected. The reported waste generation and storage data was multiplied by weighing factors to correct for the fact that only a fraction of the facilities in each group were sent questionnaires. The National Profile was generated to be statistically valid only at the national level and only for the major facility categories. It is estimated that the overall accuracy of the projected mixed waste generation rates and waste in storage are well within a factor of 2, at the 95% confidence level.

The National Profile report was not intended to provide the basis for comparison of commercial and DOE mixed waste. Hence, it did not contain enough detailed information to make the determination that DOE

has the ability to manage these waste streams within its system. Currently, DOE has its waste streams grouped into "Waste Characteristic Groups" (Appendix A). Placement of waste streams into these groups requires knowledge of both of the waste codes and some physical characteristics of the waste streams. In order to accurately assess the ability of DOE to treat the commercially generated waste streams, information was required regarding their EPA waste codes and physical characteristics. Although this information was not included in the National Profile report, it was collected as part of the facility survey/questionnaire. Access to the ORNL databases assembled from the facility's survey/questionnaires responses provided the necessary information to place the commercial waste streams into the DOE waste characteristic groups. This allowed for the determination of the common waste streams to both DOE and the commercial sector, and to identify those that are unique to only the commercial sector. ORNL did not provide the identities of any of the survey respondents.

For this report, only actual reported waste volumes for the commercially generated mixed waste streams were used where as the National Profile used estimated upper volumes. This will account for any differences found between the National Profile report (Ref. 2) and the information contained in this report. The weighing factors, standard errors, and confidence intervals established in the National Profile report were also used in this report. Detailed descriptions on the calculations of these factors can be found in Ref. 2.

Source of DOE Mixed Waste Information

The basic precondition for the efficient and economical processing and disposal of the DOE LLMW is a thorough knowledge of the quantities and compositions of the waste streams. The Mixed Waste Treatment Project (MWTP) recognized the importance of accurate waste characterization information for technology evaluations and therefore funded the MWTP date-gathering activities. (3) (All DOE mixed waste stream information contained in this report was obtained from Ref. 3. Updated information was used when available). The objective of this group was to expand upon the waste stream information so that potential treatment processes could be identified. More detailed waste characterization information was obtained by visiting all the major DOE sites.

The waste descriptions were then divided into nine classes as can be noted in the Mixed Waste Characteristic Categories (Appendix A). The major categories are aqueous liquid wastes, organic liquids, solid process residues, soils, debris materials, special wastes, inherently hazardous wastes, unknown wastes and treated materials. Most liquid wastes and solid process residues are generated in a routine manner from process operations and are subject to full RCRA regulations. They are generally homogeneous within a specific waste stream; however, it has been regularly reported that other foreign materials such as a failed pump may have been included within the process waste drums. Soils are to be the subject of a future regulation and will likely be further subdivided at that time.

Debris materials, as classified by the EPA, do not need characterization before processing because of their heterogeneity and the difficulty in characterization. The debris materials only require treatment by an appropriate technology with the process residues being included in the appropriate process residue categories. The regulations state that debris must be solid materials with an average particle size larger than 60 mm. Debris are materials that:

- have been originally manufactured or processed (specific examples include tanks, pipes, valves, appliances, scrap metal, paper, plastic, rubber, glass, concrete, brick and crushed drums);
- are plant or animal matter; or
- are natural geologic materials.

Debris can be an inseparable mixture (by simple mechanical removal processes) of such materials with soil, liquid, sludge, or other solid waste materials, but the debris must be more the 50% of the total material.

Debris cannot be process residuals (as described above).

Special wastes are those that need specific treatments or are not currently considered in the MWTP because of safety or regulatory concerns. Inherently hazardous wastes are those waste streams that cannot by treated to remove the contamination. The first objective is for the recycle of these material within the DOE or general commerce if very low level radioactive materials become releasable for general use. Unknown wastes are those wastes that cannot reasonably be included into a specific waste category because of a lack of information on that stream. The treated wastes will result from treatment processes and should be suitable for disposal. A more detailed description of the subcategories making up a waste category and the constituents of those waste streams is included in Appendix A.

Waste data gathering activities are continuing and updates to this waste stream information will be published in FY93. The quality of waste data is expected to improve as the sites complete characterization, classification, and treatment activities. However, improvements in data quality and consistency are needed. The waste data would be improved with uniformity in definitions of waste streams and classification of specific streams for each site. Currently, there are differences with respect to classification of high-level waste, transuranic waste, low-level waste, and polychlorinated byphenyls waste streams. Resolution of these differences would further improve the waste information.

EVALUATION OF LLMW INFORMATION

To adequately compare the DOE and commercial mixed waste streams, the commercial mixed waste data was placed into the DOE mixed waste characteristic groups (Appendix A). Placement of these waste streams into the waste characteristic groups is based on knowledge of their EPA codes and physical characteristics. In certain instances, when placing the commercial wastes into the DOE waste characteristic groups, deviations and assumptions were made due to lack of complete commercial mixed waste information. For example, any liquid waste that was described as being absorbed was considered to be in a solid form because different treatment methods are used for solid vs. liquid waste treatment. Also, when the commercial sector waste was described as an absorbed liquid, it was unknown whether it had been absorbed into an organic or inorganic media (DOE separates these streams) and therefore these absorbed organic liquids were kept combined as a separate waste category within the "Unknown" waste characteristic group. However, all inorganic liquids were assumed to be absorbed into an inorganic media, since this is deemed common practice. The "pure aqueous organic liquids" category was defined as having either an EPA "U" or "P" listing. Filter media was placed into the heterogenous debris waste grouping due to the mixture of sludges, paper, cartridges, and bags within this waste stream. Vitrified ash was placed into the DOE mixed waste characteristic group"treated glass". Currently, it is DOE's practice to separate elemental mercury into its own waste characteristic group, however, mercury contaminated waste streams are placed throughout the DOE waste characteristic groups. For example, broken glass and light bulbs contaminated with mercury are placed in the "glass debris" category. The mercury containing wastes are further discussed in a later section "Comparison of the Commercial and DOE Waste Sectors". "Uncategorized" describes miscellaneous wastes which fall into the waste characteristic groups, but there is insufficient information to place the waste stream into a characteristic group subcategory. A complete listing of DOE treatability groups is available in Appendix A.

Evaluation of the Commercial Waste Sector

The commercial sector generated approximately 3,863 cubic meters of mixed waste in 1990 and had approximately 1,339 cubic meters of waste stored as of 1990. The waste groups totals have been separated to reflect waste stored as of 1990 vs. waste generated in 1990. Liquid scintillation cocktails hold the largest share of the commercial mixed waste generated in 1990 (59%), followed by aqueous non-halogenated organic liquids (12%), aqueous halogenated organic liquids (8%), inorganic ash (3%), and uncategorized

combustible debris (3%). The stored commercial mixed waste as of 1990 was comprised largely of aqueous halogenated organic liquids (25%), followed by aqueous non-halogenated organic liquids (15%), uncategorized inorganic sludge, filter cakes, and residues (14%), scintillation cocktail lab packs (13%), and heterogenous filter debris (6%).

As was noted previously, commercial mixed waste production has been dispersed among academic, industrial, governmental, medical, and nuclear facilities. The facilities were placed into categories with respect to their funding source. For example, a medical facility funded by a university would be included in the academic facility category. In 1990 the academic facilities generated the largest volume of commercial mixed waste (30%), followed by the industrial (25%), governmental (22%), nuclear (16%), and medical facilities(7%). The nuclear facilities had stored the largest volume of commercial mixed waste as of 1990 (59%), followed by the industrial (23%), academic (13%), governmental (4%), and medical facilities (1%). The total volumes of waste for each facility are given below in Table 1. A detailed listing of waste streams for each facility is given in Appendix A.

Some of the facilities surveyed listed their waste minimization and source reduction techniques: placing administrative controls on procedures; proper waste segregation; utilization of biodegradable liquid scintillation fluids; usage of short-lived radionuclides; minimizing the use of liquid scintillation fluids by using new counting methods; utilization of smaller volumes of hazardous constituents in procedures; encasing lead used for biological shielding to prevent radioactive contamination; removing all packaging and non-essential material before items are brought into radiation areas; using steam or ultrasonic cleaning, grit blasting, or non-hazardous solvents to decontaminate/clean equipment; and switching from dry cleaning to a wet-wash laundry.

Table 1. Commercial Facility Waste Totals.

Commercial Facility Type	Total Waste Generated in 1990 (m^3)	Total Waste Stored as of 1990 (m^3)
Academic	962.42	175.63
Governmental	680.92	54.47
Industrial	1467.52	459.41
Medical	371.96	40.73
Nuclear	380.84	608.84
Total Waste	**3863.66**	**1339.09**

There are some situations that may create difficulties when treating the mixed waste for ultimate disposal. Although compaction is seen as waste minimization by some facilities, it is not recommended due to future waste characterization difficulties. It may also place possible limitations on treatment options, because of the need for an aggressive treatment technology that will ensure the destruction of all of the waste within the compacted mass. Creating NRC class "B" or "C" waste should be avoided when possible. The concentration of the wastes during incineration may cause the ash to be classified greater than class "C", thus limiting ultimate disposal options. Radionuclide alpha emitters are considered to be a human health risk, and should be used in limited concentrations and quantities when appropriate to avoid treatment limitations. Mixed wastes containing any of the characteristics mentioned above could make treatment more difficult, which leads to higher waste treatment (and possibly disposal) costs.

A small number of the facilities surveyed perform in-house mixed waste treatment. The academic facilities appear to be treating the largest portion of their waste in-house. Various treatment methods are utilized by all facility categories: burning for energy, incineration, neutralization, storage for decay, radioactive contaminant removal, solidification, compaction, and evaporation. Types of treatment such as burning, incineration, and evaporation have special treatment requirements. RCRA regulations and individual facility

permit requirements must be taken into account when burning or incinerating mixed waste. As far as utilizing evaporation as a treatment method, the Clean Air Act prohibits the evaporation of any waste stream that contains volatile hazardous constituents. Although certain types of treatment may be beneficial in the short-term (i.e. compaction, solidification), they may cause problems in the future when trying to treat the waste for final disposal. With final disposal in mind, it may be best to treat the wastes to meet LDR standards or not treat the waste at all.

Comparison of the Commercial and DOE Waste Sectors

The DOE generated approximately 81,000 cubic meters of mixed waste in 1990 and had approximately 179,000 cubic meters of mixed waste in storage as of 1990 (Table 2). The commercial waste generated is approximately 5% of the total U.S. mixed waste generation rate, and the commercial waste stored is approximately 1% of the total mixed waste stored in U.S. Waste streams unique to the commercial sector are uranium recovered by-products, compacted wastes, ion exchange media, explosives, halogenated organic sludge, magnesium-thorium alloy, cadmium batteries, and vitrified glass waste.

Uranium recovery by-products are generated by the DOE, but due to the complete uranium recovery process, there is no secondary uranium waste generated. The DOE has found their ion exchange media to be non-hazardous and therefore not characterized as a mixed waste. The commercial sector may be assuming their ion exchange media to be hazardous, when in fact it is not. The explosives reported by the commercial sector were described as hydrazine and TNT. It is uncertain if this information was reported accurately, due to one TNT stream being reported as having been compacted. Halogenated organic sludge does not appear to be a waste stream generated within DOE at this time. However, since the Clean Air Act now requires the reduction of ozone depleting solvents, it is assumed that solvent recycling within the DOE facilities will be generating this waste stream in the near future. At this time the DOE does not appear to be generating magnesium-thorium alloy or cadmium batteries, but these categories could be included in their uncategorized wastes.

Mercury appears to be a problematic waste for both the commercial and the DOE waste sectors. Mercury contaminated wastes appear throughout the DOE system but only the elemental liquid mercury is separated from the remaining waste categories. Although the DOE is investigating a mercury thermal desorption technology using a thermal treatment unit, mercury treatment technologies are relatively new. The various forms of mercury could allow for a range of treatment effects that are yet to be developed and demonstrated.

COMMERCIAL TREATMENT OPPORTUNITIES

This section of the report summarizes the findings of a recent investigation of the private sector's capacity to treat LLMW. The information presented below was provided to EG&G Idaho in response to a Commerce Business Daily solicitation issued July 17, 1992. It should be noted that this is vendor provided information, and any information included is subject to change based on the disposition of the facility and permits. Waste Acceptance Criteria (WAC) and current facility capabilities should be directly solicited from the vendors, for whom points of contact have been provided for assistance if needed.

Five companies hold both the necessary NRC licenses and EPA permits to handle LLMW. These include: Diversified Scientific Services, Inc. (DSSI); ENVIROCARE of Utah, Inc.; NSSI/Source & Services, Inc.; RAMP Industries Incorporated; and Quadrex Recycle Center. Scientific Ecology Group, Inc. (SEG) has filed an application with the EPA to treat LLMW.

DSSI has licensed a boiler facility to treat the liquid mixed waste categories F001-F005, as well as waste solvents in the D001 listing, and RCRA permitted D-, U-, and P-listed materials. DSSI's radioactive

Table 2. Comparison of Commercial and DOE Mixed Wastes.

Waste Stream Type	Commercial Generation (m^3/yr)	DOE Generation (m^3/yr)	Commercial Storage (m^3)	DOE Storage (m^3)
Aqueous Liquids & Slurries:				
Acidic	35.66	4,900.00	5.45	145.00
Basic	-	16.00	0.22	24.00
Neutral	19.33	49,585.00	8.54	4,989.00
Cyanide	-	1.00	-	12.00
Uncategorized	3.58	-	23.73	1,092.00
Organic Liquids:				
Aqueous:				
Halogenated	188.70	12.00	269.36	8.00
Non-Halogenated	347.36	12.00	187.71	182.00
Uncategorized	66.10	30.00	39.43	223.00
Pure:				
Halogenated	.04	1.00	0.04	16.00
Non-halogenated	1.07	4.00	1.286	9.00
Uncategorized	-	0.48	-	2.00
Uncategorized	-	450.00	-	1931.00
Solid Process Residues - Inorganic Matrix Solids:				
Paint Chips & Residues	2.98	11.00	4.61	42.00
Cemented Sludges, Ashes, & Solids	2.81	9806.00	4.55	8031.00
Particulate Inorganic Media:				
Ash	79.61	4.00	28.26	547.00
Sand Blasting Media	0.22	1.00	-	5.00
Absorbed Aqueous Liquids	15.22	3.00	15.05	370.00
Absorbed Organic Liquids	-	1.00	-	4.00
Ion Exchange Media	0.29	3.00	0.73	-
Uncategorized Particulates	-	6.00	-	104.00
Sludges, Filter Cakes & Residues:				
Low Organic Content Sludges	-	138.00	-	495.00
High Organic Content Sludges	-	43.00	-	2705.00
Sludges with Cyanide	-	-	-	-
Uncategorized Sludges	33.44	49.00	142.9	33,279.00
Salt Wastes:				
Chloride & Sulfate	-	53.00	-	53.00
Nitrate	-	-	-	4.00
Uncategorized	-	355.00	-	374.00
Uncategorized Inorganic Solids	-	4.00		2.00
Solid Process Residues - Organic Matrix Solids:				
Organic Chemicals	0.25	-	0.25	1.00
Particulate Organic Media:				
Activated Carbon	-	-	-	1.00
Organic Resins	-	-	-	10.00
Absorbed Liquid (Organic Matrix)	-	-	-	-

Uncategorized Organic Particulate	-	-	-	-
Organic Sludges:	-			
Sewage Sludges	1.91	-	0.51	403.00
HOC Sludges	1.84	-	6.10	-
Non-HOC Sludges	-	2.00	-	0.21
Uncategorized Organic Sludge	-	-	1.31	-
Uncategorized Organic Solids	-	-	-	-
Soils:				
Organic Contaminated	8.80	25.00	-	3139.00
Inorganic Contaminated	-	6.00	-	5.00
Organic & Inorganic Contaminated	-	3.00	-	16.00
Soils with Organic Debris	-	-	-	-
Soils with Inorganic Debris	-	-	-	-
Soils with Organic & Inorganic Debris	-	4.00	-	15.00
Uncategorized	0.63	3.00	-	912.00
Debris Wastes:				
Metal Debris:				
Metallic Equipment, Components, & Scrap	1.43	32.00	0.05	51.00
Uranium Chips & Turnings	-	-	-	9.00
Lead Containing Components & Materials	16.6	1.00	7.11	8.00
Cadmium Containing Components & Materials	0.03	0.02	0.03	1.00
Uncategorized	-	46.00	-	58.00
Inorganic Non-metal Debris:				
Concrete	-	-	-	-
Glass	0.07	-	0.42	-
Ceramic Crucibles & Bricks	-	-	-	-
Rocks	-	-	-	-
Uncategorized	-	1.00	-	1.00
Heterogeneous Debris:				
Filters	-	45.00	72.94	75.00
Predominantly Metal	-	9.00	-	9,959.00
Predominantly Inorganic Non-metals	-	11.00	-	987.00
Predominantly Combustible	-	64.00	-	13,354.00
Asphalt	-	-	-	-
Uncategorized	-	193.00	0.04	2,185.00
Combustible Debris:				
Plastic & Rubber:				
Leaded Gloves & Aprons	-	1.00	-	2.00
Halogenated Plastics	-	-	-	-
Non-halogenated Plastics	-	-	-	-
Uncategorized Plastic & Rubber	0.76	-	-	0.21
Wood	-	-	-	3.00
Paper & Cloth	0.22	34.00	0.22	748.00
Graphite	-	-	-	23.00
Animal Carcasses	1.71	-	2.79	4.00
Uncategorized Combustible	96.95	85.00	18.88	349.00
Special Wastes:				

Lab Packs:				
Organic	0.174	26.00	0.27	71.00
Aqueous	0.02	1.00	0.02	9.00
Solid	0.37	0.27	-	0.30
Scintillation Cocktails	2,612.53	24.00	288.18	195.00
Uncategorized	-	20.00	-	70.00
Reactive Metals:				
Bulk	-	0.21	-	14.00
Contaminated Components	-	0.44	-	6.00
Uncategorized	-	0.02	9.31	6.00
Explosives:				
Nitrated Rags & Filters	-	-	-	12.00
Uncategorized	-	-	1.34	-
Compressed Gases & Aerosol Cans	-	-	-	0.21
Inherently Hazardous Wastes:				
Liquid Mercury	7.42	1.00	64.17	5.00
Lead Shapes:				
Non-Activated	5.71	62.00	6.48	372.00
Activated	-	0.20	-	1.00
Lead with Other Materials	-	36.00	-	124.00
Beryllium	0.48	1.00	0.48	2.00
Batteries:				
Lead Acid	0.01	1.00	0.01	1.00
Cadmium	0.15	-	0.15	-
Uncategorized	-	5.00	-	0.30
Unknown Wastes:				
Liquids	-	59.00	-	207.00
Solids	-	807.00	-	6,227.00
Absorbed Organic Liquids[1]	60.01[1]	-	39.75[1]	-
Uncategorized	25.03	1,096.00	-	6,368.00
Treated Wastes:				
Cement	-	-	-	-
Glass	1.96	4.00	16.78	-
Metal	-	-	-	-
Polymer	-	-	-	-
Other Forms	-	-	-	-
Problematic Wastes:				
Compacted	27.65	-	5.47	-
Uranium Recovered By-products	57.81	-	29.26	-
Magnesium-Thorium Alloy	82.57	-	34.91	-
Mercury Contaminated[2]	20.42[2]	#[2]	83.07[2]	#[2]
TOTALS	**3,863.66**	**81,046.00**	**1,339.09**	**178,899**

[1] *It is unknown if these absorbed organic liquids were absorbed into an inorganic or organic media.*

[2] *The DOE does not list mercury-contaminated material as a separate treatability group. These materials have been extricated from other waste streams listed above for this section, due to their difficulty of treatment. The volumes listed here must be disregarded with respect to the total waste volumes, due to having been accounted for in previous waste streams.*

materials license allows for the receipt of more than 1,000 isotopes. Recently, the license as amended to allow DSSI to receive mixed wastes containing special nuclear materials and source material from government facilities. The DSSI facility will accept liquid scintillation fluid and other ignitable solvents from across the country. DSSI has a RCRA Part B permit as a TSD facility which will allow them to store waste for radioactive decay for up to 360 days. The point of contact for DSSI is Larry Hembree, Customer

Service, P.O. Box 863, Kingston, TN 37763, (615) 376-0084.

ENVIROCARE of Utah, Inc. is licensed and permitted for the disposal of radioactive mixed wastes. Their WAC includes characteristic waste codes D001-D043, listed wastes F001-F012, F019, F024, F028, F039, K011, K013, K050-K052, K061, K069, many P-listed and U-listed waste (please refer to their current WAC for details). ENVIROCARE may accept solid-phase hazardous wastes which are radioactive. Such wastes include contaminated soils and debris from government clean-up projects, process solids, sludges and other wastes. The point of contact for ENVIROCARE is Susan P. Rice, Marketing Representative, 215 S. State Street, Suite 1160, Salt Lake City, Utah 84111, (801) 532-1330.

NSSI/Sources & Services, Inc. is licensed and permitted for treatment and storage of a wide range of radioactive, hazardous and LLMW. A full list of currently acceptable waste is available upon request. Treatment capabilities of NSSI include fuel blending, consolidation of waste containers into lab packs, reconsolidation of lab packs for disposal or processing, chemical treatment, neutralization, oxidation, reduction, recycling of solvents, cleaning of particulate solids, empty drums, and equipment, centrifugation, filtration and ion exchange, solidification, shredding, separation (chemical or mechanical), absorption, solids drying, and recovery of waste chemicals for reuse or resale. The point of contact is Robert D. Gallagher, President, PO Box 34042, Houston, Texas 77234, (713) 641-0391.

RAMP Industries Inc. is licensed and permitted to treat absorbed liquids, compacted trash, contaminated plant hardware, contaminated bulk, dewatered filter media, demineralizes, dry activated waste, gaseous sources, incinerator ash, institutional lab and biological waste; liquids (solidified), liquids (aqueous and organic), liquid scintillation fluids and vials, radioactive devices of gauges, sealed sources, solidified uranium waste and sludges, transuranic material (<100 nCi/gm), non-uranium mineral extraction waste sludges, depleted uranium metals and oxides, source material, and special nuclear materials in quantities not sufficient to form a critical mass. Their treatment capabilities include volume reduction by compaction and shredding, separation, reclamation of liquid scintillation fluids, decontamination and solidification. The point of contact is John E. Lucas, General Manager, 1127 W. 46th Ave., Denver, Colorado 80211, (303) 480-1481.

Quadrex Recycle Center is licensed and permitted to treat liquid scintillation fluids and vials for fuel reclamation. They also decontaminate and recycle lead shielding and bricks (not categorized as waste). The NRC license is limited to 5 micro-curies per gram. The point of contact is John Rainey, Regional Account Manager, 109 Flint Road, Oak Ridge, Tennessee 37830-7033, (615) 482-5532.

SEG is currently licensed for the processing of radioactive waste. Their treatments include ULTRA compaction, incineration, decontamination and metal melting. Acceptable wastes include dry activated waste, lead, metals, soils and oils. For a current WAC please request directly from SEG. SEG has applied for an EPA part B permit for the treatment of LLMW (excluding incineration which will be applied for in the near future under a separate permit). The point of contact is William H. Carder, Manager Government Marketing, PO Box 2530, 1560 Bear Creek Rd., Oak Ridge, Tennessee 37831-2530, (615) 481-0222.

Caution should be used when determining and/or selecting treatment options for LLMW streams. It is the responsibility of the generator of the mixed waste to ensure that after treatment their treated waste will meet all LDR requirements. This will allow for the placement of the treated waste into an EPA/NRC permitted disposal facility. If, however, the treated waste does not meet LDR treatment standards, the waste generator will be responsible for retreating the waste stream until it meets all applicable regulations. Many times, retreatment of the waste stream is more difficult than treating the original waste form. For example, the solidification of a toxic metals waste stream into a cement matrix. Test were performed and it was found that the solidified waste form does not pass toxicity characterisitic leaching procedure (TCLP) requirements, thus requiring additional treatment. Finding a treatment method for this solidified waste matrix will be very difficult and costly. Sometimes properly storing a waste instead of partial treatment is the best option.

POSSIBLE COOPERATIVE LLMW TREATMENT AND DISPOSAL OPTIONS

The assessment of the commercial sector mixed waste streams being generated and/or stored revealed that a significant portion of these wastes are similar to the mixed waste streams being generated and/or stored by the DOE. The growing public concerns for the environment and the fears of radioactivity has place significant pressures on the DOE, the host states and compacts, and the commercial generators of mixed waste to develop safe treatment and disposal facilities for LLMW. A united approach between the DOE and the host states and compacts to solve the treatment, storage, and disposal issues associated with LLMW would prove to be beneficial to all. There is a clear need for technologies designed to meet the unique requirements for mixed waste processing and for a nation-wide integrated strategy to develop technology and deploy the capability to treat mixed waste.

Treatment Technology and Development

The DOE has currently taken the position that the commercial sector will be responsible for establishing its own treatment facilities. Currently, EPA/NRC permitted commercial treatment facilities are available to treat a significant portion of the commercially generated LLMW (i.e. liquid scintillation fluids, organic liquids, etc.) and future treatment activities are being pursued. The DOE was established as a non-competitive entity, which means they can not compete with private sector businesses. This would prohibit the DOE from treating any commercially generated waste that may have current or future commercial treatment capabilities available. Currently, commercial treatment facilities are aggressively pursing future EPA/NRC permits that will allow them to treat a greater variety of the mixed waste streams.

Reviewing the treatment facility plans for the DOE, it would appear that additional DOE treatment facilities will not be available in the near future. The Mixed Waste Integrated Program (MWIP) (4), in collaboration with the MWTP, is currently working on a systems approach to develop a multi-technology treatment facility that will be capable of handling the broad spectrum of DOE LLMW. Plans are to have a treatment facility of this magnitude built, permitted, and operational by 1997-1998. However, this is a very optimistic schedule since obtaining an EPA permit can take as long as 4-5 years and the DOE has not even started preparing the permit applications. When DOE does have a treatment facility operation, it is unlikely that they will entertain that thought of treating commercial waste until all DOE mixed waste streams are treated and the DOE is in compliance with the RCRA regulations.

However, this will not prohibit the commercial sector and the DOE from working together for the ultimate goal of establishing treatment facilities for LLMW. The DOE has spent hundreds of millions of dollars on research and development for the treatment of their mixed waste streams. This information is available to the commercial sector through technology transfer. Although technology transfer has always been an element of the activities of DOE and its laboratories, it has received increasing emphasis from U.S. policy makers in recent years as an avenue for enhancing the nation's competitiveness. Many mechanisms have been made available through which representatives of companies of all sizes and scientist and engineers in various technical disciplines at academic institutions can interact and collaborate with the DOE laboratories and facilities on LLMW treatment technologies (5).

Economic incentive does exist for an entrepreneur to build a mixed waste treatment facility since currently there are waste streams for which no treatments have been established. The Department of Energy has relaxed some of their requirements regarding sending LLMW to commercial facilities for treatment. Examples of this are the Hanford Reservation sent spent radioactive organic solvents to DSSI for treatment and ORNL has been sending radioactive contaminated metals to SEG for recycling. With this new philosophy developing within the DOE system, a commercial LLMW treatment facility may potentially have DOE waste streams added to their treatment throughput. This would aid in lowering the treatment cost due to the increased volume of waste needing treatment.

Delisting Activities Pursued by DOE

Waste streams exist within the commercial sector that appears to be able to meet the delisting requirements from the RCRA LDR regulations. For example, the vitrified ash waste stream that is being generated by a nuclear utility. This waste stream was listed as hazardous due to the toxic metals contained in the ash. By vitrifying this ash, the toxic metals become part of the glass matrix. This is a very stable waste form that meets the TCLP requirements and one would suspect that it could potentially be delisted from the RCRA Land Disposal Restriction Requirements. However, delisting this waste streams would be extremely costly on a low volume basis.

The DOE's MWIP is currently pursuing an aggressive delisting project that will prepare a delisting strategy plan for the DOE and apply this strategy to delist specific DOE mixed waste streams that are treated in a vitrifier/melter treatment process. The intent is to lead into the concept that if you can ensure the destruction of the hazardous constituent and/or the stabilization of the toxic constituents into the waste matrix that the treatment process itself can be delisted. The blanket delisting of treatment processes for DOE waste streams could potentially be applicable to commercial waste streams being treated in a similar matter.

Siting of a LLMW Disposal Facility

The greatest impact the DOE can have in helping the commercial sector with their LLMW problems is by siting a LLMW Disposal Facility within the DOE system. With the current problems facing the host states and the state compacts in siting commercial disposal facilities for just low-level waste, it would seem an almost impossible task of siting, permitting, and operating a disposal facility for LLMW.

The amount of waste being generated and stored in the commercial sector is so small that it would not make any sense to build more than one disposal facility (Table 3). The placement of this disposal facility would be a tremendously difficult task with the "not in my backyard" philosophy circulating in today's culture. Even if a LLMW disposal facility could be placed, the disposal cost for placing waste in such a facility would be hundreds of dollars per cubic feet. As treatment costs and disposal costs increase, illegal disposal of mixed wastes could occur or force small business generating mixed wastes to shut down. This could potentially put the nation at risk since the largest generators of mixed waste are not the nuclear utilities as popular beliefs suggest, but are the industries and academic facilities. Forcing these entities to not product mixed waste would shut down a large portion of research being conducted by the pharmaceutical industries and medical research being conducted by academic facilities. With the real threats of aids and cancer facing our populations, the reduction of pharmaceutical and medical research could have significant consequences on our futures.

The DOE accepting commercial mixed waste for ultimate disposal is not a new concept. DOE is currently responsible for disposing of the commercially generated high-level wastes at DOE facilities. The DOE is going to have to create LLMW disposal facilities for their own mixed wastes. With the DOE currently generating 95% of the mixed waste in the U.S. and storing 99% of the stored mixed waste in the U.S., it makes sense that they become responsible for siting LLMW disposal facilities. In fact the portions of the commercial sectors mixed waste is so small that a DOE disposal facility will not need to expand its disposal capacity to absorb the commercial waste.

DOE is pursuing investigations into defining an ultimate waste form(s) for final disposal at its facilities. Although this study has not been complete, it appears that DOE is likely to select vitrified waste and other enhanced forms for its waste disposal criteria. This means that if the commercial sector sends its mixed waste to a DOE disposal facility, the waste will need to be in an enhanced form before DOE will accept it for ultimate disposal. Currently a commercial vitrifier/melter is not operational. Each DOE facility also has established their own Performance Assessment Criteria which requires extensive pathway analysis to

Table 3. Commercial Mixed Waste Distribution per EPA Region*.

EPA Region	Weighted Volume Generated (cubic meters)	Weighted Volume Stored (cubic meters)
Region #1	290	95
Region #2	868	163
Region #3	651	222
Region #4	25	14
Region #5	732	298
Region #6	327	143
Region #7	17	4
Region #8	74	84
Region #9	467	246
Region #10	61	6
Region #11	3	9
Region #12	130	29
Region #14	119	31
Region #17	91	3
Region #18	8	0
TOTALS	**3,863 m^3**	**1,347 m^3**

* *Information contained in this table was obtained from surveys/questionnaires received for the National Profile Report. This national survey was not designed to accurately represent mixed waste in the EPA regions, but was designed to accurately represent the 5 facility categories. Caution must be employed in interpreting the data in ways other than those for which the survey was designed.*

be performed to ensure the waste form's integrity. This ensures that the disposed waste will not create future environmental and health effects.

Another issue that would be resolved if DOE would site a LLMW disposal facility is that commercial mixed waste treatment facilities could start treating Class B, C, and Greater than Class C waste streams without fear of concentrating the radionuclides in the waste residues. Currently, mixed waste treatment facilities are very careful when treating particular radionuclides and waste with high concentrations of radioactivity. The reason is that some treatment processes actually produce a more concentrated waste residue than the initial waste being treated. It is possible to treat Class A waste and have Class B residues left for ultimate disposal. The disposal cost is proportionate to the radionuclide concentration.

CONCLUSIONS

A comparison of the data shows that DOE mixed waste volumes, both for current generation and for storage, are much greater than those in the commercial sector. While this may have been obvious, it is important because it may point out the need for DOE to play a lead role in the solutions to the mixed waste dilemma. The siting, permitting, and construction of treatment and disposal facilities is very expensive and, in some cases, may be prohibitive. The decision of DOE to collaborate with the commercial sector in the treatment or disposal of mixed waste will be a primary factor in determining the unit costs for management of this waste. An additional point related to this conclusion is that of legal liability. DOE is subject to the same enforcement provisions associated with mixed waste management as the private sector. While it might be desirable for DOE to take a role in the management of commercial mixed waste, it cannot do so at the risk of compromising its own ability to meet its legal obligations. Any actions that DOE might consider in this regard will have to meet this test.

Analysis shows that there is little substantial difference between the mixed waste being managed in the commercial sector, and that of DOE. This leads to the observation that if DOE implements technological solutions to its mixed waste issues, these solutions should be generally appropriate for the private sector.

Another conclusion is directed at identifying the potential role for DOE in the management of commercial mixed waste. It appears that there are two principal areas of potential involvement. These are:

- Transfer of technology. There is significant potential for DOE to share its experience in the development, testing, and operation of potential treatment processes. These activities are often high cost,high financial risk activities that are not attractive to the private sector. Delisting is another area in which DOE could cooperate with the private sector.

- Providing access to DOE disposal capacity. While it is possible that DOE will make use of commercial treatment facilities, it is highly unlikely that DOE would dispose of its mixed waste in a commercial disposal site. From the standpoint of the low incremental cost of receiving the commercial waste and the minimal impact of the small volume of commercial mixed waste that would be disposed, it seems that such action would be appropriate.

While these conclusions may be legally, regulatively, and technically valid and reasonable, it is necessary to point out that there are significant political and policy issues that must be addressed. These include issues of equity among the States and DOE sites. Most of these issues exist both on the commercial side and within the DOE complex, and must be resolved regardless of the level of cooperation between DOE and the States. Additionally, while this request has been made of DOE, there have been no broadbased activities conducted to identify and involve all potential interested stakeholders in the process.

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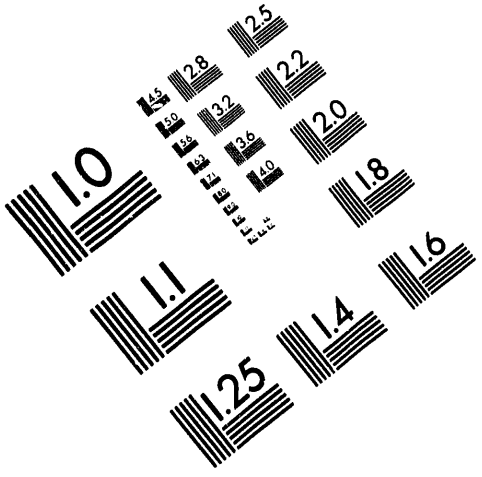

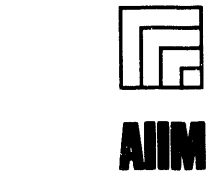

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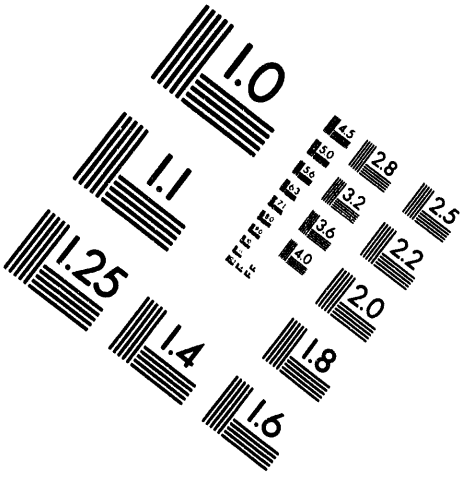

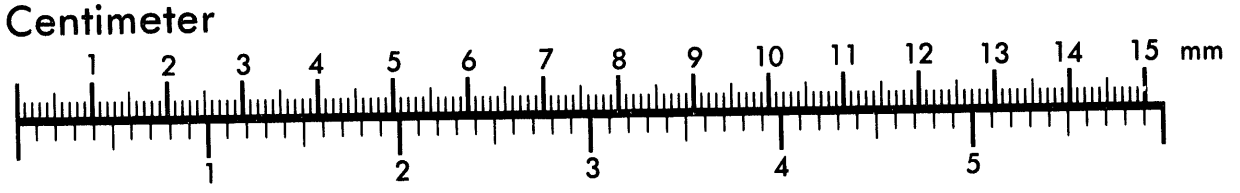

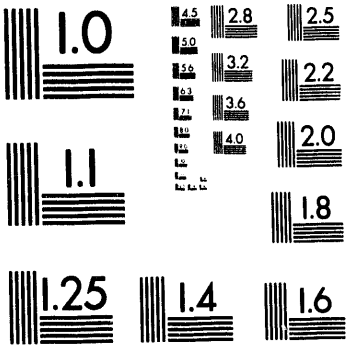

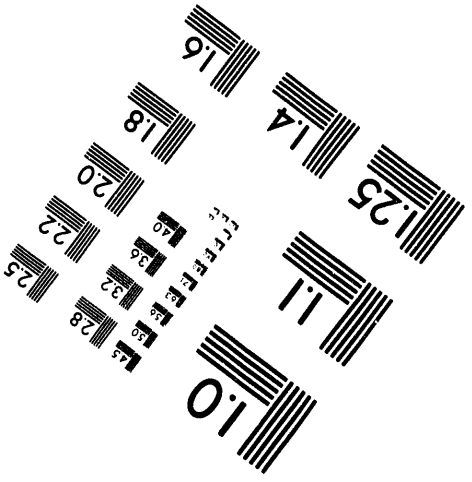

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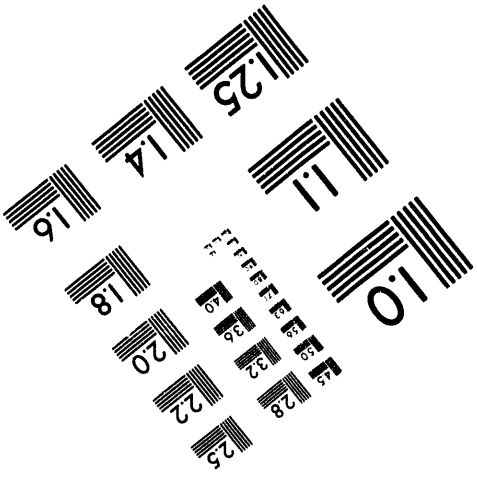

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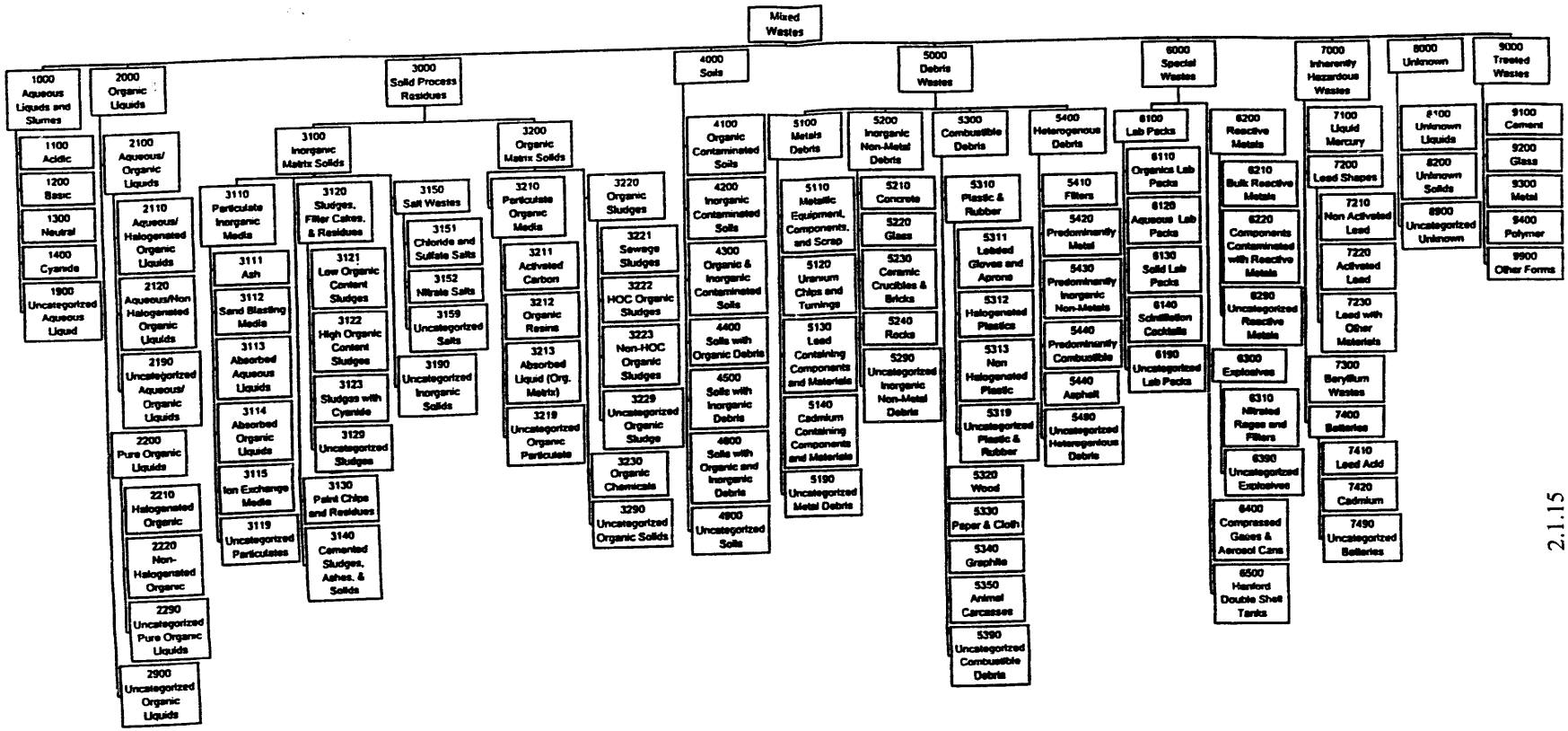
Mixed Wastes
1000 Aqueous Liquids and Slurries
1100 Acidic
1200 Basic
1300 Neutral
1400 Cyanide
1900 Uncategorized Aqueous Liquid
2000 Organic Liquids
2100 Aqueous/ Organic Liquids
2110 Aqueous/ Halogenated Organic Liquids
2120 Aqueous/Non Halogenated Organic Liquids
2190 Uncategorized Aqueous/ Organic Liquids
2200 Pure Organic Liquids
2210 Halogenated Organic
2220 Non-Halogenated Organic
2290 Uncategorized Pure Organic Liquids
2900 Uncategorized Organic Liquids
3000 Solid Process Residues
3100 Inorganic Matrix Solids
3110 Particulate Inorganic Media
3111 Ash
3112 Sand Blasting Media
3113 Absorbed Aqueous Liquids
3114 Absorbed Organic Liquids
3115 Ion Exchange Media
3119 Uncategorized Particulates
3120 Sludges, Filter Cakes, & Residues
3121 Low Organic Content Sludges
3122 High Organic Content Sludges
3123 Sludges with Cyanide
3129 Uncategorized Sludges
3130 Paint Chips and Residues
3140 Cemented Sludges, Ashes, & Solids
3150 Salt Wastes
3151 Chloride and Sulfate Salts
3152 Nitrate Salts
3159 Uncategorized Salts
3190 Uncategorized Inorganic Solids
3200 Organic Matrix Solids
3210 Particulate Organic Media
3211 Activated Carbon
3212 Organic Resins
3213 Absorbed Liquid (Org. Matrix)
3219 Uncategorized Organic Particulate
3220 Organic Sludges
3221 Sewage Sludges
3222 HOC Organic Sludges
3223 Non-HOC Organic Sludges
3229 Uncategorized Organic Sludge
3230 Organic Chemicals
3290 Uncategorized Organic Solids
4000 Soils
4100 Organic Contaminated Soils
4200 Inorganic Contaminated Soils
4300 Organic & Inorganic Contaminated Soils
4400 Soils with Organic Debris
4500 Soils with Inorganic Debris
4600 Soils with Organic and Inorganic Debris
4900 Uncategorized Soils
5000 Debris Wastes
5100 Metals Debris
5110 Metallic Equipment, Components, and Scrap
5120 Uranium Chips and Turnings
5130 Lead Containing Components and Materials
5140 Cadmium Containing Components and Materials
5190 Uncategorized Metal Debris
5200 Inorganic Non-Metal Debris
5210 Concrete
5220 Glass
5230 Ceramic Crucibles & Bricks
5240 Rocks
5290 Uncategorized Inorganic Non-Metal Debris
5300 Combustible Debris
5310 Plastic & Rubber
5311 Leaded Gloves and Aprons
5312 Halogenated Plastics
5313 Non Halogenated Plastic
5319 Uncategorized Plastic & Rubber
5320 Wood
5330 Paper & Cloth
5340 Graphite
5350 Animal Carcasses
5390 Uncategorized Combustible Debris
5400 Heterogenous Debris
5410 Fillers
5420 Predominantly Metal
5430 Predominantly Inorganic Non-Metals
5440 Predominantly Combustible
5440 Asphalt
5490 Uncategorized Heterogenous Debris
6000 Special Wastes
6100 Lab Packs
6110 Organics Lab Packs
6120 Aqueous Lab Packs
6130 Solid Lab Packs
6140 Schmillation Cocktails
6190 Uncategorized Lab Packs
6200 Reactive Metals
6210 Bulk Reactive Metals
6220 Components Contaminated with Reactive Metals
6290 Uncategorized Reactive Metals
6300 Explosives
6310 Nitrated Rages and Fillers
6390 Uncategorized Explosives
6400 Compressed Gases & Aerosol Cans
6500 Hanford Double Shell Tanks
7000 Inherently Hazardous Wastes
7100 Liquid Mercury
7200 Lead Shapes
7210 Non Activated Lead
7220 Activated Lead
7230 Lead with Other Materials
7300 Beryllium Wastes
7400 Batteries
7410 Lead Acid
7420 Cadmium
7490 Uncategorized Batteries
8000 Unknown
8100 Unknown Liquids
8200 Unknown Solids
8900 Uncategorized Unknown
9000 Treated Wastes
9100 Cement
9200 Glass
9300 Metal
9400 Polymer
9900 Other Forms

2.1.15

Appendix A

Aqueous Liquids and Slurries

Title	DOE Description	Modified Description for Commercial Waste Streams
Aqueous Liquids and Slurries	Aqueous solutions or slurries that have less than 1% organic content. Solids must be pumpable, but can be up to about 35-40% of the mass.	Percentage of organic content in waste was not specified.
Acidic	These solutions have a pH of less than 2 and a RCRA code of D002. They are typically general waste waters, plating line solutions, and electropolishing activities. The acid may be of any type. Most common acid types are nitric, sulfuric, and hydrochloric.	Percentage of organic content in waste was not specified.
Basic	These are solutions with a pH of greater than 12.5 and a RCRA code of D002. They are generated from a variety of activities. They can result from neutralization of acidic streams.	Percentage of organic content in waste was not specified.
Neutral	Solutions with a pH from 2 to 12.5. One source is condensate from evaporators.	Percentage of organic content in waste was not specified. May contain metals and inorganic/organic liquids.
Cyanide	Any Stream that contains cyanide as a significant component. Solutions will generally be basic.	Percentage of organic content in waste was not specified.
Uncategorized Aqueous Liquid	Aqueous liquid streams for which insufficient information is available to further characterize or streams that contain mixtures of waste categories.	Percentage of organic content in waste was not specified. Inadequate written description or EPA waste codes given to characterize the waste.

Organic Liquids

Title	DOE Description	Modified Description for Commercial Waste Streams
Organic Liquids	Liquid streams that are either essentially a pure organic stream or those streams that contain both aqueous and organic materials. Solids must be pumpable, but can be up to 35-40% of the mass.	Percentage of organic content in waste was not specified.
Aqueous/Organic Liquids	Liquid streams that contain mixtures of aqueous and organic liquids with contents of 1% or more of organic liquids but less than about 99% organic.	Percentage of organic content in waste was not specified.
Aqueous/Halogenated Organic Liquids	Liquid streams that contain mixtures of aqueous and halogenated organic liquids with contents of 1% or more of organic liquids but less than about 99% organic.	Percentage of organic content in waste was not specified.
Aqueous/Non-Halogenated Organic Liquids	Liquid streams that contain mixtures of aqueous and non-halogenated organic liquids with contents of 1% or more of organic liquids but less than about 99% organic.	Percentage of organic content in waste was not specified. Oils not contaminated with solvents were placed in this category.
Uncategorized/Aqueous Organic Liquids	Liquid streams that contain mixtures of aqueous and uncategorized organic liquids.	Percentage of organic content in waste was not specified.
Pure Organic Liquids	Liquids with only organic materials.	"Pure" was determined by any "U" or "P" EPA waste codes specified.
Pure Halogenated Organic	Nearly pure organic liquids containing more than trace (~1000 ppm) levels of halogens (e.g., F, Cl, Br, etc.). Contaminated freon is one specific waste stream. High level PCB wastes are also a potential waste stream.	"Pure" was determined by any "U" or "P" EPA waste codes specified.
Pure Non-Halogenated Organic	Nearly pure organic liquids free of more than trace (~1000 ppm) levels of halogens (e.g., F, Cl, Br, etc.). Oils, hexon, and methanol are typical streams.	"Pure" was determined by any "U" or "P" EPA waste codes specified.
Uncategorized Pure Organic Liquid	Organic liquids that cannot be categorized as halogenated or non-halogenated.	
Uncategorized Organic Liquid	Organic liquids for which insufficient information is available to determine the aqueous content and whether the stream is more than trace halogenated.	

Solid Process Residues

Title	DOE Description	Modified Description for Commercial Waste Streams
Solid Process Residues	These materials are typically residues from process operations such as waste water cleanup or process operations, or are listed wastes.	
Inorganic Matrix Solids	These are materials that have an inorganic matrix or content such that they would have a high residue from incineration. They may contain both hazardous organics and metals. They may also contain either aqueous or organic interstitial liquids.	
Particulate Inorganic Media	Fine particulate wastes. Typical sources are ash from incinerators, dusts, sand blasting residue, vermiculite, and ion exchange media.	
Ash	Materials generated from the incineration of radioactive wastes. It includes both bottom ash, fly ash, and other solid residues.	
Sand Blasting Media	Particulate material (generally course sand or glass) used to decontaminate or clean radioactively contaminated materials.	
Absorbed Aqueous Liquids	Inorganic materials such as clay, vermiculite, or diatomaceous earth added to absorb aqueous liquids or placed in drums to absorb liquids if internal containers leak.	The media the aqueous liquids were absorbed into is not specified.
Absorbed Organic Liquids	Inorganic materials such as clay, vermiculite, or diatomaceous earth added to absorb aqueous liquids or placed in drums to absorb liquids if internal containers leak.	The media the organic liquids were absorbed into is not specified.
Ion Exchange Media	Inorganic materials that have been used to remove ions from liquid streams.	
Uncategorized Particulates	Particulate materials that cannot be assigned to any of the above categories or is a mixture of such materials including absorbed liquids or materials that have some trap materials.	
Sludges, Filter Cakes, and Residues	These materials are generally from wastewater cleanup or from settling ponds. They may contain organic materials in limited quantities from laundry or other sources. Heavy metals are present in some sludges. Equipment, filters, and other materials have occasionally been included with some drums.	
Low Organic Content Sludges	Sludges with less than 1% of hazardous organic materials.	Percentages of organic content in the waste were not specified. Process knowledge was used to determine the general range of organic content

Solid Process Residues

Title	DOE Description	Modified Description for Commercial Waste Streams
High Organic Content Sludges	Sludges with greater than 1% hazardous organic material. The organics can be either halogenated or non-halogenated materials.	Percentages of organic content in the waste were not specified. Process knowledge was used to determine the general range of organic content.
Sludges with Cyanide	Sludges that contain cyanides as more than a trace concentration.	
Uncategorized Sludges	Sludges with unknown levels of organic content or sludges with other components such as paper filter media.	
Paint Chips and Residues	New or removed paint. The paint may have some liquid content either as original paint or as a paint stripper; it may also be paint chips. Painting equipment would be a debris waste.	
Cemented Sludges, Ashes, and Solids	Sludges or solids that contain cement or other solidifying agents either as a water absorber or that are mixed with cement or solidifying agents to produce a homogenous solid waste, but do not yet meet disposal requirements. Final Treated cemented materials are a cement waste.	
Salt Wastes	Salt wastes.	
Chloride and Sulfate Salts	Evaporated or process salt that may contain more than trace concentrations of sulfate and chloride or other halogens.	
Nitrate Salts	Evaporated or process salts that are predominantly nitrate salts.	
Uncategorized Salt Wastes	Salt wastes with unknown chloride, sulfate or nitrate salts or are non-chloride, non-sulfate, or non-nitrate.	
Uncategorized Inorganic Solids	Inorganic solid waste streams that cannot be further characterized or is a mixture of materials.	
Organic Matrix Solids	These are materials that have an organic matrix or base structure. They may have some liquid present, but will not leave a large residue when incinerated.	
Particulate Organic Media	Particulate organic media including spent organic resins, spent carbon filters used in wastewater cleanup, or particulate organic material used to adsorb organic or aqueous liquids.	
Activated Carbon	Particulate activated carbon that has often been used for removal of organic materials from off-gas streams or liquid streams.	
Organic Resins	Organic based resins that have been used in wastewater treatment or other applications.	
Absorbed Liquids (Organic Matrix)	Liquids absorbed on a particulate organic matrix such as cellose or pulverized corn cobs.	The media the aqueous liquids were absorbed into is not specified.

Solid Process Residues

Title	DOE Description	Modified Description for Commercial Waste Streams
Uncategorized Organic Particulate	Particulate materials or media that cannot be categorized above or that is a mixture of the above materials.	
Organic Sludges	Organic based sludges of various types.	
Sewage Sludges	Sludges generated in treating wastewater from animals or people.	
HOC Organic Sludges	Halogenated organic containing materials that cannot be poured from a drum at room temperature for treatment as an organic liquid.	
Non-HOC Organic Sludges	Non-Halogenated organic containing materials that cannot be poured from a drum at room temperature for treatment as an organic liquid.	
Uncategorized Organic Sludges	Organic sludges which could not be categorized because of it being a combination of materials or because of its unknown chemistry.	
Organic Chemicals	Drums of unused organic chemicals.	"Unused" was determined by the specification of a "U" or "P" listed EPA waste code.
Uncategorized Organic Solids	Materials that cannot be included into any of the above organic solid categories or is a combination of categories.	

Soils

Title	DOE Description	Modified Description for Commercial Waste Streams
Soils	Soils contaminated with hazardous materials and radioactivity. They may contain up to 50% debris. Streams with more than 50% debris would be a debris waste. This group is subdivided as noted below, however, it may be modified when specific EPA regulations are promulgated.	Percent of debris was not specified.
Organic Contaminated Soils	Soils contaminated with hazardous organics from activities such as spills, drains, and wastewater treatment. May contain up to 5% debris materials.	Percent of debris was not specified.
Inorganic Contaminated Soils	Soils contaminated with hazardous inorganics from activities such as spills, drains, and wastewater treatment. May contain up to 5% debris materials.	Percent of debris was not specified.
Organic and Inorganic Contaminated Soils	Soils contaminated with both hazardous organic and inorganic materials from activities such as spills, drains, and wastewater treatment. May contain up to 5% debris materials.	Percent of debris was not specified.
Soils with Organic Debris	Soils contaminated with more than 5% hazardous organic debris materials from activities such as spills, drains, D&D, and previous waste disposal actions. These streams may also contain organic or inorganic hazardous materials.	Percent of debris was not specified.
Soils with Inorganic Debris	Soils contaminated with more than 5% hazardous inorganics debris from activities such as spills, drains, D&D, and previous waste disposal actions. These streams may also contain organic or inorganic hazardous materials.	Percent of debris was not specified.
Soils with Both Inorganic and Organic Debris	Soils contaminated with more than 5% of either or both hazardous organic and inorganic debris from activities such as spills, drains, D&D, and previous waste disposal actions. These streams may also contain organic or inorganic hazardous materials.	Percent of debris was not specified.
Uncategorized Soils	Soils contaminated with unknown materials or with a combination of the above series of soil waste categories.	Percent of debris was not specified.

Debris Waste

Title	DOE Description	Modified Description for Commercial Waste Streams
Debris Wastes	Wastes that meet the EPA criteria for debris. Debris materials are divided into four groups as either metal, inorganic non-metal, combustible, or mixtures of materials (heterogeneous). If the wastes are dominant in one type of material, it should be classed as that material. Otherwise, it is heterogeneous.	
Metal Debris	Streams that generally have a metal content greater than about 95%.	
Metallic Equipment, Components, and Scrap	General metallic items that have been used in process operations or maintenance. Typical items include piping, pumps, metal filters, traps, wire, and fixtures. It is anticipated that the metal content is greater than about 95%.	
Uranium Chips and Turnings	Uranium metal components or particulate materials with other types of materials to reduce uranium reactivity.	
Lead Containing Components and Materials	Metallic lead-containing materials, including gloveboxes, lead wool, lead base solder materials, or lead components used in radioactive processes. It also includes lead shapes mixed with other materials or lead encapsulated in other metals. This stream does not include lead acid batteries or pure lead shapes used as shielding.	
Cadmium Containing Components and Materials	Components formed from cadmium or contain a significant fraction of cadmium. This stream does not include cadmium batteries.	
Uncategorized Metal Debris	Metallic components that cannot be classed as a specific metal debris waste stream because of lack of knowledge or because it contains multiple categories.	
Inorganic Non-Metal Debris	Debris streams composed of about 95% inorganic non-metal materials.	
Concrete	Concrete materials removed from building or roadways.	
Glass	Items composed primarily of glass. It may be process equipment, laboratory equipment, window materials, vessels, bottles, or light bulbs, if metallic components are removed. This stream may include leaded glass. The glass may contain small amounts of organic, metal, or other inorganic materials.	

Debris Waste

Title	DOE Description	Modified Description for Commercial Waste Streams
Ceramic Crucibles and Bricks	Crystalline or glass materials used as crucibles or refractories.	
Rocks	Rocks and gravel that have a particle size greater than 60 mm.	
Uncategorized Inorganic Non-Metal Debris	Non-Metallic items that cannot be classed as a specific Inorganic Non-Metal Debris waste stream because of lack of knowledge or because it contains multiple categories.	
Combustible Debris	Specific waste streams that contain more than about 95% combustible materials.	
Plastic and Rubber	Plastic and rubber such as sheeting, containers, gloves, gaskets, and components of benelex or plexiglass.	
Leaded Gloves and Aprons	Rubber materials that contain a high fraction of lead and lead compounds.	
Halogenated Plastics	Plastics, such as PVC, that contain halogens as part of their chemical structure.	
Non-Halogenated Plastics	Plastics, such as polyethylene, that are free of halogenated materials.	
Uncategorized Plastic and Rubber Materials	Materials that cannot be separated into any of the above categories or that contain a mixture of such materials types.	
Wood	Wood items such as structural timbers, boxes, or pallets.	
Paper and Cloth	Paper and cloth items such as protective clothing, and items used to wipe up contamination or absorb liquids. Wipes may contain some absorbed organic and aqueous liquids.	
Graphite	Crucibles or components of graphite or carbon.	
Animal Carcasses	Dead animal or parts of animals. Most animals will have been used in testing and may contain chemical agents such as lime or formaldehyde to stabilize them.	
Uncategorized Combustible Debris	Uncharacterized combustible or mixtures of combustible materials in the above categories.	Materials that would normally be treated by incineration and do not fall into any of the categories listed.
Heterogeneous Debris	Mixtures of metals, non-metals, combustibles, soils, and process residues that can be classified as debris.	

Title	DOE Description	Modified Description for Commercial Waste Streams
Filters	HEPA filters, and other process filters. Filters are contaminated with fine particulate. HEPA filters may be either wood or metal frame. Particulate filter media would be process residues.	
Predominantly Metal	Debris materials that contain more than about 50% but less than about 95% inorganic non-metals with other debris.	
Predominantly Inorganic Non-Metal	Debris materials that contain more than about 50% but less than about 95% inorganic non-metals with other debris.	
Predominantly Combustible Debris	Debris materials that contain more than about 50% but less than about 95% combustible materials with other non-combustible debris.	
Asphalt	Asphalt materials from roadways or other sources and contain both tar and gravel.	
Uncategorized Heterogeneous Debris	Heterogeneous debris that cannot be further characterized, or does not contain a dominance of metals, non-metals, or combustible debris.	

Special Wastes

Title	DOE Description	Modified Description for Commercial Waste Streams
Special Wastes	These waste streams will require specific treatment methods that are not expected to be common with other waste types. It also includes waste streams for which treatment capacity may not be initially established as part of the Mixed Waste Treatment Project.	
Lab Packs	This category includes more than just the conventionally identified lab packs. It includes all wastes that contain liquids in containers with surrounding packing materials such as vermiculite. Lab packs contain mixtures of chemicals in drums. Chemicals are mostly solid but can contain liquids in bottles.	
Organic Lab Packs	Lab packed materials that contain organic liquids.	
Aqueous Lab Packs	Lab packed materials that contain aqueous liquids.	
Solid Lab Packs	Lab packed materials that do not contain liquid materials.	
Scintillation Cocktails	Solutions used for scintillation counting. Solutions are most often in the original glass or plastic analysis bottles.	May be bulk liquid or liquid in vials, but not absorbed liquids.
Uncategorized Lab Packs	Lab packed materials that could be classified as more than one waste code from the Lab Packs series or that have insufficient information available to further classify.	
Reactive Metals	Reactive metals are typically sodium metal or alkali metal alloys, but can also be particulate fines of aluminum, uranium, zirconium, or other pyrophoric materials and may be mixed with stabilizing materials.	
Bulk Reactive Metals	Nearly pure reactive metals in containers. They may have various types of impurities, but the bulk of materials is reactive metal and can be treated in a bulk processing system.	
Components Contaminated with reactive Metals	Piping, pumps, and other materials that have reactive metal contamination. The bulk of the material is not reactive metals, but the reactive metals require treatment before disposal.	

Special Wastes

Title	DOE Description	Modified Description for Commercial Waste Streams
Uncategorized Reactive Metals	Non-alkali metal reactive or mixtures of reactives.	
Explosives	Any material that may explode during normal or extreme handling.	
Nitrated Rags and Filters	Rags that have absorbed nitric acid and then been left in storage.	
Uncategorized Explosives	Materials that may be explosive that are not nitrated rags or filters.	
Compressed Gases and Aerosol Cans	Aerosol cans and gas cylinders with gases of any composition. It is expected that the containers will be pressurized. Non-pressurized containers would be a debris waste.	
Hanford Double Shell Tanks	Wastes in Hanford Double Shell Tanks.	

Inherently Hazardous Wastes

Title	DOE Description	Modified Description for Commercial Waste Streams
Inherently Hazardous Materials	Materials that are composed of inherently hazardous materials.	
Liquid Mercury	Liquid mercury pourable from containers. Will include drums of waste that contain elemental mercury within a container.	
Lead Shapes	Bulk lead materials that are separable from other wastes in the form of bricks, sheets, or unique components.	
Non-Activated Lead	Lead bricks, shipping casks, or shielding materials. The lead should only be surface contaminated.	
Activated Lead	Lead activated from it's use in radiation fields such as in reactors or accelerators where it can be activated.	
Lead with Other Materials	Lead bricks or shapes in drums of waste with other inorganic or organic type materials. The lead should be a shape that can be decontaminated and can be easily separated from the other wastes.	
Beryllium Wastes	Beryllium metal chips or materials contaminated with more than trace levels of beryllium. It should be a P015 RCRA waste.	
Batteries	These are generally lead and cadmium type batteries, but will include other types as well.	
Lead Acid Batteries	Lead acid batteries.	
Cadmium Batteries	Cadmium type batteries.	
Uncategorized Batteries	Other types of batteries or unclassifiable batteries.	

Unknown Wastes

Title	DOE Description	Modified Description for Commercial Waste Streams
Unknown	Waste materials that cannot reasonably be classified into one of the other categories based on available information or streams for which the available information is conflicting.	
Unknown Liquids	Liquid wastes that cannot be categorized as aqueous or organic liquids.	
Unknown Solids	Solid materials that cannot be categorized.	
Uncategorized Unknown	Materials that cannot be categorized.	

Treated Wastes

Title	DOE Description	Modified Description for Commercial Waste Streams
Treated Wastes	Wastes that have been treated to meet the land Disposal Restriction.	
Cement	Cement type waste forms including grouts and cements of various types.	
Glass	Wastes that have been converted to a vitreous type waste form.	
Metal	Metal waste forms that have been consolidated or decontaminated and are ready for disposal or recycle.	
Polymer	Organic type waste forms including polyethylene, bitumen, resins, and other organic binders.	
Other Forms	Final waste forms that are not classed as either a cement, glass, metal, or polymer. It would include amalgamated mercury and microencapsulated lead.	

DEVELOPMENT OF TREATMENT TECHNOLOGIES FOR THE PROCESSING OF U.S. DEPARTMENT OF ENERGY MIXED WASTE

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ABSTRACT. Waste contaminated with chemically hazardous and radioactive species is defined as mixed waste. Significant technology development has been conducted for separate treatment of hazardous and radioactive waste, but technology development addressing mixed-waste treatment has been limited.

In response to the need for a comprehensive and consistent approach to mixed-waste technology development, the Office of Technology Development of the U.S. Department of Energy (DOE) has established the Mixed Waste Integrated Program. The program is identifying and evaluating treatment technologies to treat present and estimated future mixed wastes at DOE sites. The status of the technical initiatives in chemical/physical treatment, waste destruction/stabilization technology, off-gas treatment, and final waste form production/assessment is described in this paper.

INTRODUCTION

U.S. Department of Energy (DOE) mixed waste is contaminated with both chemically hazardous and radioactive species. Management of mixed waste requires treatment that must meet the standards established by the U.S. Environmental Protection Agency (EPA) for the specific hazardous constituents while also providing adequate control of radionuclides. Technology development conducted for radioactive waste and for hazardous waste has been significant, but development specifically addressing mixed-waste treatment issues has been limited. Technology has not been designed, developed, demonstrated, or tested to produce a low-risk final waste form.

A comprehensive and consistent approach to the complex issue of mixed-waste management has been established by the DOE Office of Environmental Restoration and Waste Management. The Office of Waste Management established the Mixed Low-Level Waste Program with the primary objective of identifying and implementing the optimum treatment, storage, and disposal options for mixed waste (1). The Office of Technology Development established the Mixed Waste Integrated Program to develop mixed-waste treatment technology in support of the Mixed Low-Level Waste Program.

A driving force for the development of mixed-waste treatment technology is provided by EPA regulations. The primary purpose of the Land Disposal Restrictions (LDRs) is to prohibit the placing of untreated wastes in or on the land when there is a better treatment alternative. EPA has established treatment standards for all characteristic and listed wastes that either require the use of specified treatment technologies or require

that the wastes be treated to EPA-established concentration limits for the hazardous constituents (2). The concentration limits are based on the use of the best demonstrated available technology (BDAT) even though the waste can be treated by any technology (as long as the waste is treated to the same or lower levels as the BDAT).

After EPA established the BDAT for a waste, it then established an effective date for the LDRs based on a nationwide availability of BDAT capacity. This assessment placed DOE mixed wastes in a category of waste that had a May 8, 1992, LDRs compliance deadline. However, several issues have delayed DOE compliance with the LDRs schedule. These issues include, but are not limited to, transportation of waste to distant treatment sites, the matrix within which the hazardous components are found, and complications of treatment attributed to the presence of the radioactive components. Throughout the DOE complex, the mixed-waste problem is significant because definitive treatment standards have not been established and few disposal facilities are available (3, 4). In addition, the treatment that is available is limited in its capability and capacity. The problem has been summarized as "a lack of existing proven technology to treat and dispose of mixed waste to meet treatment standards" (5). Without capability and capacity to treat mixed wastes, DOE sites have been forced to store untreated waste. However, the LDRs also prohibit the storage of restricted wastes except when necessary to accumulate sufficient quantities to properly treat, recover, or dispose. Therefore, the sites that have not pursued or are not pursuing a Federal Facility Compliance Agreement with EPA and the state in which they are located may be in violation of the LDRs.

The Federal Facility Compliance Act of 1992 (FFCA) amends the Resource Conservation and Recovery Act (RCRA) to waive sovereign immunity for federal facilities, permitting the assessment of fines and penalties on DOE for violations of RCRA. Several of the provisions of FFCA address violations of the LDRs storage prohibition for mixed wastes by federal facilities (6). The act does not invalidate existing agreements but does establish a 3-year timeframe for facilities to develop plans to come into compliance with the LDRs. The items these plans must contain include the treatment technologies that exist for the mixed wastes in question and, if none exists, the schedule for identifying and developing the needed technologies. A national approach to developing the needed technologies can draw the resources of the DOE complex and private industry together, thus significantly reducing costs.

A total of approximately 179,000 m^3 of mixed waste that does not comply with specific requirements established by EPA is being stored at DOE sites (7). In addition, the generation of mixed waste continues at the rate of 81,000 m^3/year. DOE wastes cover the spectrum of possible waste management concerns. In fact, DOE has classified 751 individual waste streams for 34 sites into 9 broad waste matrix categories.

One strategy being used by the Mixed Low-Level Waste Program is to "establish a standardized approach to mixed waste management activities throughout the DOE system that is cost effective, and sets a technically sound standard of excellence for environmental protection in the DOE waste management programs" (1). To implement this strategy, the Mixed Waste Treatment Project has combined waste streams that require similar processing steps to establish a generic baseline mixed-waste treatment scheme using currently available technologies. The logic for processing mixed waste is comprehensive and covers the range of wastes requiring treatment within the DOE complex. By using a comprehensive national approach to the mixed-waste problem rather than focusing on a specific site, the major treatment needs have been identified (Fig. 1).Commercially available equipment has been identified for the majority of processing steps; however, no techniques were currently available for some steps in the processing logic. Furthermore, this baseline treatment scheme includes disposal of radioactive material, recycle of decontaminated material, and incineration activities for which system requirements have not been established. Technology development is required to investigate the application of existing technologies to the treatment of mixed waste and to the development of integrated treatment modules. Further development is required to obtain data to support the establishment of system requirements and to meet the identified needs of the treatment scheme. Additionally, there are opportunities to improve upon the baseline treatment process by applying

innovative waste treatment operations. New technologies under development have the potential for major process impacts by simplifying and increasing the throughput rate of the baseline treatment process. Technologies will be developed to enhance or improve the baseline technologies such that the implemented treatment scheme is more cost effective, has better performance, and has lower risk than the baseline.

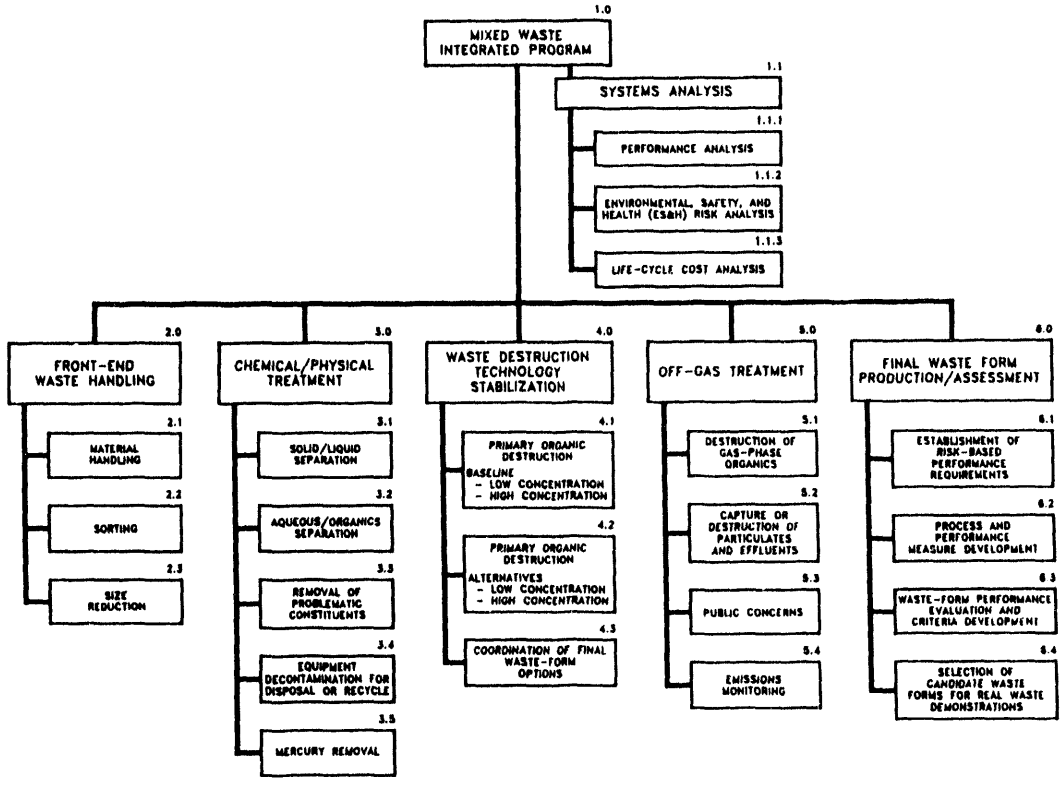

Figure 1. Mixed Waste Integrated Program technology areas.

A systematic approach is being employed to determine how the baseline treatment scheme should be modified to incorporate innovative technologies. An example of the application of this systems approach is seen by comparing Figs. 2 and 3. Fig. 2 illustrates the baseline flow sheet for thermal treatment technologies. An innovative alternative to this baseline thermal treatment system includes a plasma arc furnace that has the potential to treat numerous waste streams in one unit operation (Fig. 3). The two systems are being compared for performance (i.e., material and energy balance, operability, maintainability, and reliability); risk (i.e., environmental, safety, and health risk); and life-cycle cost. Those subsystems that are superior to commercially available subsystems will be included in mixed-waste treatment facility design.

Needs for technology development have been broadly categorized into the following technical areas: front-end waste handling, chemical/physical treatment, destruction/stabilization technology, off-gas treatment, and final waste form production/assessment. Specific technology development needs have been identified by analyzing the Mixed Waste Treatment Project baseline flow sheet as described above. The goal of the Mixed Waste Integrated Program is to develop a suite of appropriate technologies that will treat mixed waste to acceptable disposal criteria and provide design and reliability data on the schedule required to support implementation of mixed-waste treatment. The status of the technical initiatives in the technical areas of chemical/physical treatment, destruction/stabilization technology, off-gas treatment, and final waste form production/assessment is described below (8,9,10,11).

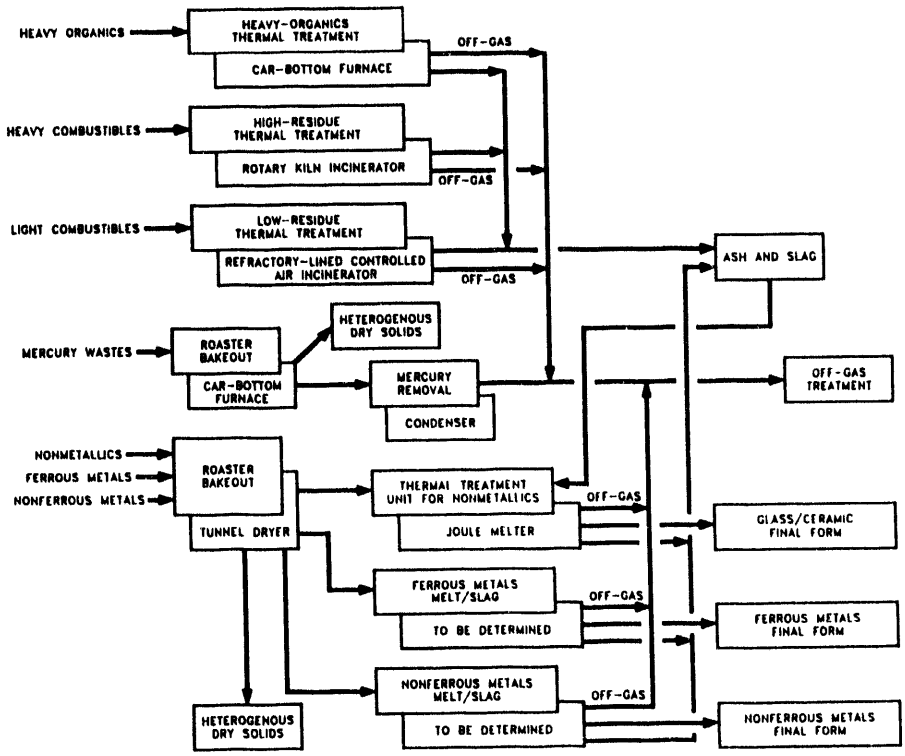

Figure 2. Mixed Waste Integrated Program flow sheet - thermal baseline.

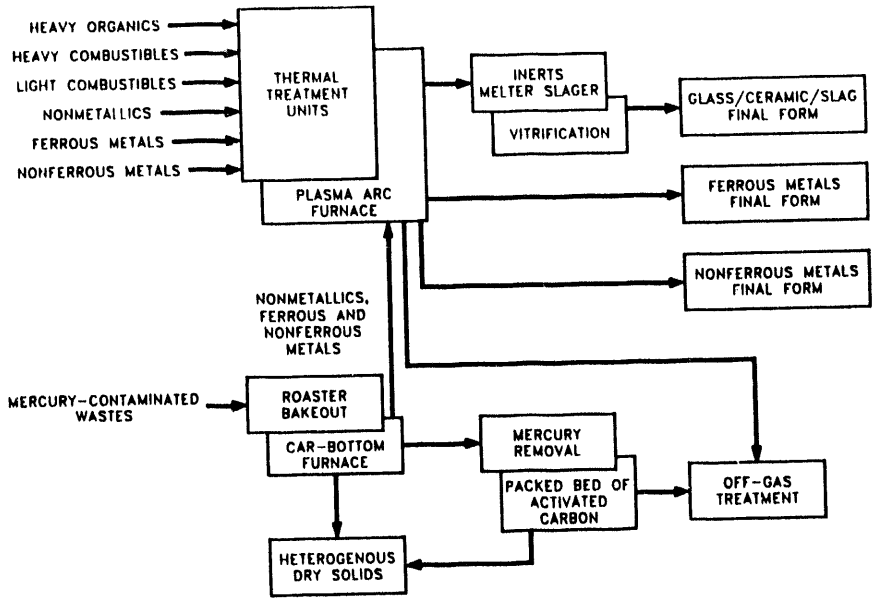

Figure 3. Mixed Waste Integrated Program flow sheet - thermal treatment.

CHEMICAL/PHYSICAL TREATMENT

Chemical/physical treatment technology for DOE mixed waste involves five processing lines in the prototypical treatment scheme: (1) aqueous processing, (2) organics processing, (3) mercury processing, (4) wet solids processing, and (5) decontamination (12). Sources of feed to th processes are both external and internal recycle. The primary goals of the chemical/physical treatment systems are (1) the separation of solid and liquids, (2) the separation of organics and water, (3) the removal of problematic constituents (such metals and salts), (4) the removal of mercury, and (5) the decontamination of containers and their lids or other parts for disposal or recycling.

Aqueous solutions or slurries containing less than 40% suspended solids and less than 1% organics are classified as aqueous liquids. The baseline treatment for aqueous liquids includes the separation of solids and liquid using filters and centrifuges, the removal of dissolved organics using activated carbon, the removal of dissolved solids by precipitation processes, the evaporation of clean water from a liquid concentrate containing salts and other solids, and the production of a wet solid from in-process generated slurries using a wiped film evaporator (13,14).

Current technology development efforts in aqueous processing center on the need for more effective methods to remove salts (especially chlorides, nitrates, and sulfates) and alternatives to the baseline treatment scheme. Salts contained in concentrate from evaporation are problematic to downstream processing steps such as thermal processing, final waste forms, and off-gas treatment. A nitrate destruction/removal process that produces a ceramic final form is being evaluated to replace this salt-removal step (15). Alternatives to the other baseline processes in aqueous processing are being considered to reduce waste generation and eliminate high-pressure processes. One approach uses steam stripping to remove organics; another incorporates fractional crystallization to process the bulk feed. Both alternatives would conceptually produce clean water and eliminate the need for both activated carbon and wet air oxidation.

Solutions or slurries that contain greater than 1% organics and less than 40% suspended solids are classified as organic liquids. Organic liquids include spent solvents, liquids in scintillation vials, and slurries. The baseline treatment for organic liquids includes separation of low-content and high-content organic streams, preparation of the low-content organic stream for wet air oxidation, and preparation of the high-content organic stream for thermal destruction. Current technology development needs in organics processing are focused primarily on the removal of submicron particles from the high-content organic stream prior to thermal destruction. Particulate material can cause erosion problems in the burners and increase the particulate loading to the off-gas treatment system.

All DOE mixed wastes have the potential for being contaminated with mercury. In the baseline mercury processing scheme, mixed waste that contains mercury is segregated and then processed in a bakeout oven operated at approximately 400°C. Mercury is volatized at this temperature, and vapor condensed overhead contains mercury, water, and other condensable materials. Mercury is separated by decantation and refined by batch distillation. The clean mercury can then be recycled and the distillation still bottoms processed into a final waste form.

Mixed waste classified as wet solids includes sludges, adsorbed liquids, resins, salts, and cemented sludges. This waste represents the largest fraction of the mixed-waste inventory. The baseline processing scheme consists of low-temperature vacuum drying for temperature-sensitive materials and high-temperature (approximately 200°C), ambient-pressure drying for nonsensitive materials. Current technology development efforts in wet solids processing center on the need for effective methods to remove salts. The salts in this stream are present in a solid matrix of widely varying composition. One alternative being considered involves leaching of salts from the wet solids by washing with water.

Materials that require decontamination include empty containers, lids, metal drum parts, and heterogeneous

waste that is considered debris. Bins and other recyclable containers that are used for internal transport of material also require decontamination before reuse. The baseline approach is to utilize aqueous-based cleaning solutions to effect the decontamination. Aqueous solutions are collected for treatment and recycled or directed to aqueous processing as needed for disposal. Technology is needed for the remote decontamination of materials and for a decontamination process that will not create a large secondary waste stream.

WASTE DESTRUCTION/STABILIZATION TECHNOLOGY

DOE is investigating the use of thermal treatment technologies for waste destruction and stabilization (16). Innovative technologies, loosely defined as those technologies that are not currently being used on a large scale to treat wastes, are being demonstrated, and issues regarding full-scale operation are being resolved. Development of the following processes is currently in progress: metal-melting technologies, photochemical organic destruction processes, thermal reactor processes, and plasma arc incineration. Metal-melting technologies are basically adapted from the metals industry (e.g., induction furnaces, plasma arc melters) and the glass industry (e.g., fuel-fired and joule-heated melters). Although the operating principles for these processes are not new, there is only limited operational experience in the waste management area. In addition, new concepts in melting processes are being researched as waste management tools (e.g., the microwave melter) (17).

Melter technologies hold the promise of being highly effective for waste treatment because the ash residue may not require additional treatment prior to disposal. The final waste form is physically and chemically stable and will likely pass regulatory performance standards. Because of the high temperature of melting operations, melters can be used to destroy residual organics. Process modifications will be required to ensure the destruction of organic material during the metal-melting process.

Melters are ideally suited for inorganic waste streams such as inorganic oxides and elemental metals. Furthermore, the chemistry in the melt can be reducing or oxidizing depending on the type of waste form desired. When processing oxides, the final waste form will be a glass or a ceramic, primarily depending on the rate of cooling. When processing metals, the melt will form a top layer of slag and a bottom layer of molten metal. The slag can then be separated from the molten metal, allowing for the recycle of the molten metal. Depending on operating parameters, it is possible to oxidize the majority of the radionuclides in the waste so that the radionuclides become part of the slag, resulting in a decontaminated molten metal.

Research and development are needed in the waste destruction area. Generally, these needs can be classified as requiring more operational experience, better materials of construction, improved materials-handling techniques, less waste pretreatment, control of the chemistry in the process, and detailed analysis of the resulting residue and off-gas to determine the constituents that are in the process effluent streams.

OFF-GAS TREATMENT

DOE is evaluating air pollution control equipment (18) for use in treatment of gaseous effluent from mixed-waste stream processing based on criteria generally relevant to DOE facilities. These criteria include primary pollutant removal, secondary waste stream generation, safety, versatility, experience, simplicity, and cost. The preliminary evaluation resulted in ranking the spray dryer absorber best for acid gas removal, high-efficiency particulate air filters best for particulate removal, activated carbon adsorption best for removal of both toxic metals and residual hydrocarbons, and selective catalytic reduction best for nitrogen oxide abatement. However, selection of off-gas components for a given application is highly dependent on waste streams, location, and thermal technology.

A systematic analysis is used to select the appropriate off-gas system for a given waste stream. For the purpose of illustration, the expected performance of two hypothetical DOE waste streams and thermal treatment technologies is presented here.

The first waste stream is defined to contain a large variety of waste types (i.e., solids, sludges, and liquids) and is therefore suitable for processing in a rotary kiln, which is a versatile thermal treatment device. The rotary kiln process is mated with wet and semidry off-gas systems in series. The wet off-gas system is designed with a rotary atomizer as the principal component and will accomplish excellent removal of acid gases and good removal of particulate. Other pollutants would not be affected, or the removal efficiency for such pollutants is not known. The semidry off-gas system for the rotary kiln is designed with a spray dryer absorber/baghouse combination for good removal efficiency of acid gases and excellent removal efficiency of particulate and toxic metals.

The second waste stream is defined to contain a large percentage of contaminated soils and inorganic constituents, making it amenable to the plasma arc system, which will not only destroy the organic constituents but also vitrify and stabilize the inorganic constituents. The plasma arc process is mated with wet and dry off-gas systems in series. The wet off-gas system incorporates a venturi/packed-bed scrubber combination to accomplish excellent acid gas and nitrogen-oxides removal and moderate removal of particulate and toxic metals. The dry off-gas system incorporates selective noncatalytic reduction followed by dry sorbent injection and the use of a baghouse. This system accomplishes moderate acid gas and NO_x removal and excellent removal of toxic metals.

Particular areas in which further research and development are necessary include treatment and disposal of secondary wastes, ability to remove multiple pollutants, mass-transfer rates, optimization of multiple air pollution control devices used in an integrated off-gas train, process control, catalyst activity and resistance to degradation, and materials of construction for air pollution control devices.

FINAL WASTE FORM PRODUCTION/ASSESSMENT

Treatment of mixed waste is intended to protect human health and the environment from risks associated with the release of hazardous and radioactive components from the waste. DOE Order 5820.2A requires for each disposal site a performance assessment, which shows by analysis that the waste treatment process and other disposal controls adequately meet this objective. At present the assessment does not credit the waste form with any capacity to restrict contaminant mobility; all containment is attributed to physical barriers such as vaults. In order to rate the waste form as a physicochemical barrier to contaminant release, performance criteria must be developed. Criteria can be based solely on regulatory requirements, solely on technical parameters, or on a combination of the two. The combination approach has been selected, recognizing that current regulatory criteria do not address all of the properties of a waste form that determine its ability to reduce contaminant mobility and acknowledging that the properties measured may not, in fact, be indicative of the performance of the waste form in the specific disposal setting. The most important technical requirement affecting whether a waste form can be disposed of is the long-term stability of the waste form in the disposal setting. This information is critical in developing the performance assessment, which documents the ability of the entire waste control system to prevent unacceptable releases. Tests to measure and predict release rates of hazardous and radioactive constituents need to be developed and verified for long-term stability. There is a need to establish uniform testing requirements for waste form performance for both short- and long-term stability. Compositional flexibility, minimal volume increase, and low unit cost are all desirable properties of waste forms. Difficulties experienced with the long-term integrity and performance of traditional waste form technologies (e.g., cementation, grout) have led DOE to consider evaluation of technologies for production of enhanced waste forms (e.g., glass, ceramics) with the expectation that these waste forms will exhibit comparatively superior performance characteristics (e.g., leach resistance, durability), which will facilitate eventual disposal.

DOE is evaluating the use of the following groups of final waste forms for mixed waste disposal: hydraulic cement, sulfur polymer cement, glass, ceramics, and organic binders. The current status of the development of enhanced waste forms has been determined, gaps and deficiencies in what is known about technologies have been identified, and a course of action to alleviate these deficiencies has been recommended (18).

Evaluation of vitrification processes for mixed-waste streams is in progress in an attempt to assess alternative technologies for inclusion in the proposed prototype treatment plant for mixed waste. Vitrification-related treatability studies include research on the following waste streams: incinerator ash (including air pollution control equipment sludge), wastewater treatment sludge, soils, and off-specification cemented wastes. The treatability studies will involve (1) characterization of the wastes, using laboratory-scale or "crucible" studies to identify appropriate glass compositional formulations and additive requirements; (2) engineering-scale process studies (e.g., steady-state operation) of small-scale melters to identify process concerns; and (3) pilot-scale demonstrations of the process in an integrated fashion including feed and air pollution control system evaluation.

CONCLUSION

The DOE Office of Technology Development has established a national approach to technology development for mixed-waste treatment. This multifunctional approach reduces duplication of technology development effort as compared with a site-specific approach. A comprehensive approach to the solution of DOE mixed radioactive and toxic waste problems includes an analysis of alternative waste treatment systems. The implemented treatment schemes will be more cost effective, have better performance, and have lower risk than baseline technologies.

The regulatory drivers found in the LDRs and the FFCA have mandated treatment and development schedules that will be difficult for all the sites to achieve on an individual basis. A coordinated effort among all the sites will be required so that each site can take advantage of the efforts taking place at other sites.

Technology development for mixed-waste treatment has been categorized by evaluating the required treatment steps. A prototypical mixed-waste treatment scheme includes unit operations in the following technical categories: front-end waste handling, chemical/physical treatment, waste destruction/stabilization technology, off-gas treatment, and final waste form production/assessment. DOE has initiated technology development activities in each of these technical areas. This paper describes significant progress to date and additional research needs in the areas of waste destruction/stabilization technology, off-gas treatment, and final waste form production/assessment.

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DEVELOPING WASTE SEPARATIONS TECHNOLOGIES IN THE UNDERGROUND STORAGE TANK - INTEGRATED DEMONSTRATION PROGRAM

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ABSTRACT. The principal objective of the Underground Storage Tank - Integrated Demonstration (UST-ID) Program is the demonstration and continued development of technologies suitable for the remediation of USTs. The most promising new technologies are selected for demonstration, testing, and evaluation. The objective is the eventual transfer of new technologies as a system to full-scale remediation at U.S. Department of Energy (DOE) complexes and sites in the private sector. Technologies under development in the UST-ID Program are targeted toward use in remediation actions at the following five DOE participant sites: Hanford, Fernald, Idaho, Oak Ridge, and Savannah River. Combined, these participant sites have more than 300 USTs containing more than 100 Mgal of high-level and low-level radioactive liquid waste.

This paper focuses on the Waste Separations and Pretreatment area of the UST-ID, summarizing the currently funded technology development projects. In this area, several "compact processing units" are being developed to effect near-term demonstration and deployment of promising processes in actual tank environments. The compact processing units design and development approach is summarized. A number of programmatic issues are discussed, including onsite and offsite transportation of potentially contaminated processing systems, containment design criteria, including applicable codes and standards, and operation and maintenance of such systems in a developmental testing environment.

INTRODUCTION

Production of nuclear materials has been a major mission of the U.S. Department of Energy (DOE) and predecessor agencies for the last 50 years. These activities have contributed to a substantial accumulation of hazardous, radioactive, and mixed wastes. In 1989, the DOE established the Office of Environmental Restoration and Waste Management. This Office coordinates and manages the DOE's remediation, waste minimization, and environmental compliance activities. It also has responsibility for managing waste generated by current operations. Within this Office is the Office of Technology Development, which is responsible for providing technology improvements. The integrated demonstration process is a critical component in the evolution of technology improvements. Integrated demonstrations have been established to efficiently bring the best technologies to bear on the common needs of multiple DOE sites. One such need is resolution of the actions required for final closure and disposal of liquid (including sludge and salt cake), radioactive, and chemical wastes that have been transferred to underground storage tanks (USTs).

Technologies must be developed to remediate USTs containing high-level, low-level, transuranic, and mixed wastes at five DOE participant sites: Fernald, Idaho National Engineering Laboratory (INEL), Oak Ridge National Laboratory (ORNL), Savannah River Laboratory (SRL), and Hanford (the host site). The DOE has made a commitment to remediate the USTs and related near-field environments that are not in compliance with state and federal regulations and to treat and dispose of the wastes in accordance with

currently accepted practice. However, the cost of cleanup of these tanks is prohibitive using some of the current baseline technologies. Furthermore, major gaps exist in key technology areas.

The Underground Storage Tank - Integrated Demonstration (UST-ID) Program was created in February 1991 with a principal objective to develop and demonstrate technologies that will provide improvements or alternatives to the remediation baseline plan. This demonstration is necessary to enable a final decision on the disposal of underground tank wastes, soils, and ancillary equipment. The UST-ID is led by the DOE, Richland Operations Office (RL), and Westinghouse Hanford Company (WHC). The program is focusing on the needs of several of the participating sites simultaneously, thus ensuring that technologies under development are applicable to more than one site, which will minimize the cost of development.

Activities currently included within the UST-ID are (1) characterization, (2) retrieval transfer and interim storage, (3) waste separation and pretreatment, and (4) low-level waste (LLW) form development. These investigations include all regulatory interfaces necessary for actual field testing of the potential technologies and the regulatory acceptance of the technologies used.

The foundation of the program is the technology base available from within the DOE and from external industrial and institutional programs that can be applied to the UST remediation efforts. The UST-ID secures the active involvement of private industry, universities, and other government agencies, where appropriate, through the following: (1) developing collaborative partnerships, (2) licensing of technologies, (3) fostering technical personnel exchanges, (4) effecting consulting agreements, and (5) promoting shared use of scientific facilities.

The UST-ID management structure, Fig. 1, has been developed to manage the programmatic activities in an effective and responsible manner for the DOE. The integrated demonstration coordinator uses the direction provided by DOE-Headquarters (HQ) and the Hanford Site technical program officer to develop a comprehensive program. Through the Hanford Site technical program officer, the coordinator serves as the lead interface with the DOE, Office of Technology Development. The integrated demonstration coordinator arranges the delivery of the technologies into the program from a variety of sources. This includes working with the Program Planning Group, the Technical Support Groups, and other integrated demonstration coordinators from across the DOE complex to define each supporting task necessary to meet the program objectives and with the Office of Technology Development to plan for task funding and initiation.

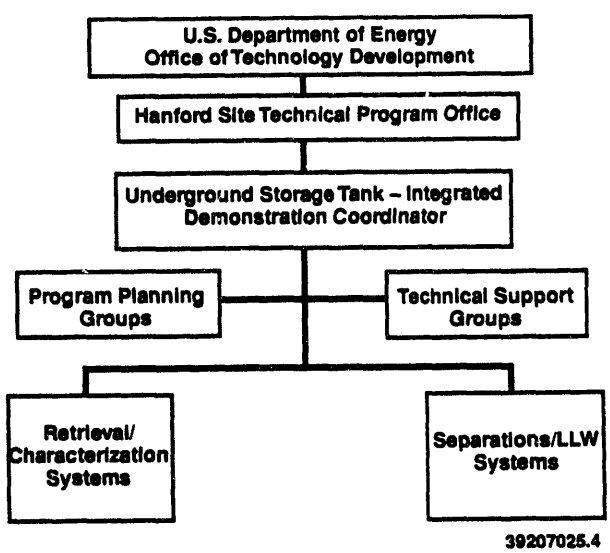

Figure 1. Underground Storage Tank - Integrated Demonstration Program Management Structure.

THE DOE TANK WASTE LEGACY

The UST-ID Program is the most complex of the integrated demonstration programs. The program's scope includes 334 USTs constructed of various materials including stainless steel, concrete, and concrete with carbon steel liners. The tanks typically have an overburden layer of soil ranging from a few feet to tens of feet. The capacity of the tanks varies from 19 to 3,785 m^3 (5,000 to 1,000,000 gal). At present 381,800 m^3 (101 Mgal) of high-level and low-level radioactive liquid wastes are contained within the tanks (Fig. 2) (1). Of the participant site inventories, the tanks at the Hanford and Savannah River Sites contain most of the waste - 60% and 34%, respectively.

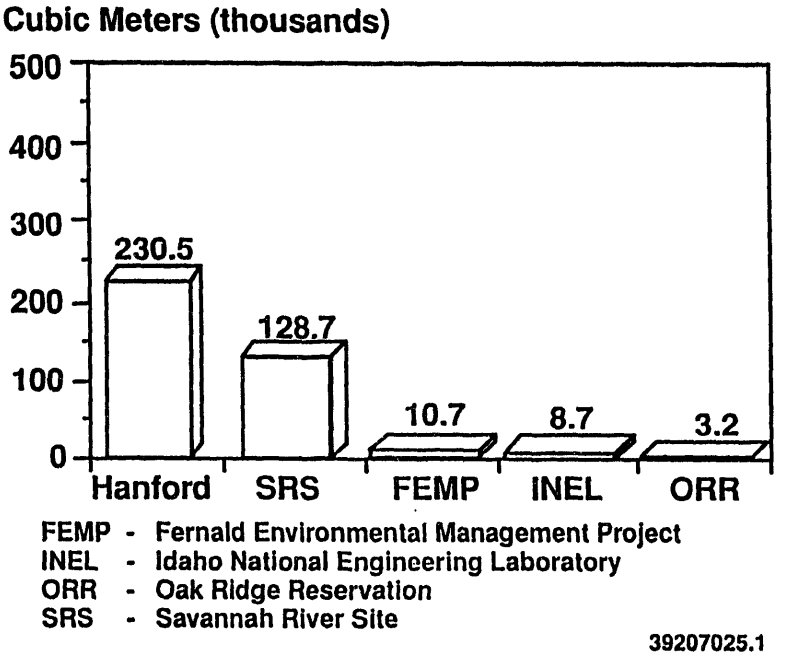

Figure 2. Total waste volumes at Underground Storage Tank - Integrated Demonstration Program participant sites.

The waste contains a wide variety of hazardous and nonhazardous chemical components, including sodium salts, acids, metal oxides, and other heavy metals. Approximately half of the waste is composed of sodium nitrate and nitrites. Large amounts of metal oxides, especially aluminum and iron oxides, are present also. The 784 MCi of radionuclides are distributed primarily among the transuranic (TRU) elements and some fission products (^{137}Cs and ^{90}Sr) (Table 1). In-tank atmospheric conditions vary in severity from near ambient to temperatures over 93 °C (200 °F). Some tanks occasionally contain potentially explosive gas mixtures. Tank void-space radiation fields can be as high as 10,000 rad/h.

WASTE SEPARATIONS AND PRETREATMENT TECHNOLOGIES

This section of the UST-ID Program deals with the initial separation of waste before the creation of the final waste form. Pretreatment to remove and concentrate high-level components of tank wastes is an important waste management option. The incentive exists because the components are generally quite dilute in the waste streams. Hence, significant reductions in toxicity and volume might be achieved through their removal. Associated with the volume reductions in TRU waste and high-level waste (HLW) are significant potential reductions in final waste disposal and tank remediation costs.

Table 1. Underground storage tank radionuclides content.

Radionuclides	Activity (Ci)	Mass	
		(kg)	(lb)
^{238}U	551	1,635,840.0	3,606,130.0
^{235}U	199	92,163.0	203,180.0
^{239}Pu	173,573	2,803.0	6,177.0
^{137}Cs	200,416,290	2,318.0	5,110.0
^{90}Sr	218,969,620	1,587.0	3,498.0
^{90}Y	182,080,000	0.3	0.7
^{144}Ce	3,453,414	1.1	2.4
^{147}Pm	25,420,600	26.0	58.0
Others	153,966,714	385.4	852.0
Total	784,480,961	1,735,123.8	3,825,008.1

The UST-ID Program is maintaining close communication with the operating waste management (EM-30) programs at the participant sites. For example, the overall plan and strategy for pretreatment and disposal processing of Hanford Site tank wastes is under re-evaluation by the EM-30 Program and its operating contractor, WHC, Tank Waste Remediation System (TWRS) Division. Representatives from the UST-ID Program are participating in this process. Several overall concepts are under evaluation. The concepts range from a relatively simple sludge wash operation followed by an enhanced vitrification plant to an extended pretreatment concept known as the "Clean Option." This area of the UST-ID is in need of an overall strategic approach to address the technology development needs at the Hanford Site and the other participant sites as well. Accordingly, a new Separations Steering Group (SSG) has been formed with site representation and a primary near-term mission to develop this strategic plan. The process to develop the strategic plan may result in the need to change direction on some of the currently funded projects in this area of the UST-ID.

The currently funded wast separation and pretreatment tasks are dedicated primarily to development of "pretreatment" processes that will reduce the volume of waste requiring final processing and long-term storage or disposal as HLW, LLW, or TRU waste. The development approach has been grouped into three primary areas based on the three major categories of tank wastes: (1) supernates, (2) salt cakes, and (3) sludges. Processes under evaluation and targeted for potential demonstration include cesium and strontium extraction, alkaline sludge washing, calcination, dissolution, transuranic extraction (TRUEX), and several others. The Compact Processing Units (CPU) will be designed and built to effect near-term deployment and demonstration of selected processes.

Comprehensive Sludge/Supernate Demonstration, Test, and Evaluation

This set of tasks will focus on developing a comprehensive sludge/supernate processing flowsheet for the contents of radioactive waste stored in USTs throughout the DOE complex. Primary emphasis will be on Hanford Site tank wastes.

Sludge Partitioning and Treatment. A key aspect to pretreatment of tank wastes will be to partition and treat troublesome constituents on a production basis. This task will be performed to develop an optimal waste minimization process that has low risk and is cost effective, environmentally sound, and reliable. Tests will be conducted using existing technologies to determine the optimal subset that can work together to achieve

a cost-effective production-scale waste minimization process. These same processes are under investigation by the Hanford TWRS for possible incorporation into its technology baseline.

This task will address (1) the separation of sludges from supernates, (2) washing of the sludge and pretreatment of the dissolvable portions, (3) acid dissolution of the sludge, and (4) partitioning (separating and concentrating) of TRU components. In this task, a comprehensive sludge processing flowsheet will be developed and tested in an ORNL hot cell using hot wastes from the ORNL Melton Valley Storage Tanks (MVSTs). The comprehensive flowsheet developed in this task will provide the basis for design and operation of a pilot-scale waste processing facility, which in turn will provide the design basis for a production-scale facility to process the MVST wastes.

This work is being done in a hot cell using actual tank wastes from the MVSTs at ORNL. This radioactive waste is similar to Hanford Site tank wastes and is easily retrievable, allowing these "hot" verification tests to be conducted more quickly at ORNL than at the Hanford Site.

TRUEX Model Development and Validation. This task will provide for transfer of the Generic TRUEX Model (GTM) to other DOE preapproved participants. These participants will perform tests to validate the GTM using actual waste. Argonne National Laboratory (ANL) will provide consultation, as required by the validating participants. Validation testing will be conducted by ORNL.

The DOE's USTs harbor large volumes of waste, which contain TRU components, at Hanford and other sites. The TRUEX process is being developed to separate these TRU components from the nonradioactive contents, thereby greatly reducing the volume of HLW to be treated and disposed of.

The ORNL, as part of its radioisotopes program, refines and collects significant amounts of americium from irradiated SRL targets. This program, known as "Mark 42," is funded by DOE-Defense Programs and DOE-Office of Energy Research. The americium recovery program produces an acid waste that is good feed for piloting TRUEX. Using a hot cell at ORNL, personnel conducting this task and personnel involved in the Mark 42 program will conduct the validation runs using this "hot" waste as feed. This waste stream is different in chemical and radiochemical composition compared to the Hanford Site wastes; therefore, these tests will be used for validation of the model only. Additional testing will be required for GTM application for the Hanford Site wastes. The fiscal year (FY) 1993 activities will focus on collecting and analyzing samples. Model validation is planned for FY 1994.

Technical Interchange with the Commissariat L'Energie Atomique (France). Several countries (including France, Japan, and the United Kingdom) are pursuing programs directed at improving the chemical processes associated with the reprocessing of spent nuclear fuels. As part of these efforts, many of the countries are developing new technologies for separating specific fission products and actinides from the waste streams. These activities are directed toward reducing the amount and radiotoxicity of the waste. It is in the national interest to establish and expand our collaborative agreements with the major international organizations involved in such separation technology research and development activities.

In this task, a technical staff member will be assigned to one of the French Commissariat L'Energie Atomique (CEA) sites for a period of approximately one year. The assignee will work as a member of a CEA development team working on research and development activities within mutually agreed upon technical areas. The primary area of interest is the Diamine process, a novel separation process that will separate TRU materials in a manner similar to TRUEX, but using a different flowsheet. The DOE is interested in evaluating this alternative treatment method. Also, the assignee would develop a broad understanding of the French waste management programs as a whole.

Calcination/Dissolution Process Development

A series of full-scale demonstrations is under way at a vendor site for calcining simulated Hanford Site waste using plasma arc technology to determine the feasibility of calcining in a production-scale process. Based upon the results of the first test, subsequent tests using varying simulant waste recipes and plasma system operating parameters will be conducted during FY 1993. A primary objective is to identify the combination of chemical dissolution and thermal processing that will destroy 99% each of the nitrates, the organics, and the ferrocyanide compounds. A favorable feature of the plasma arc process is that it would also separate the TRU materials into a relatively small solid volume. Fig. 3 presents the current calcination system concept, which includes a plasma torch cupola, offgas system, and input/output handling.

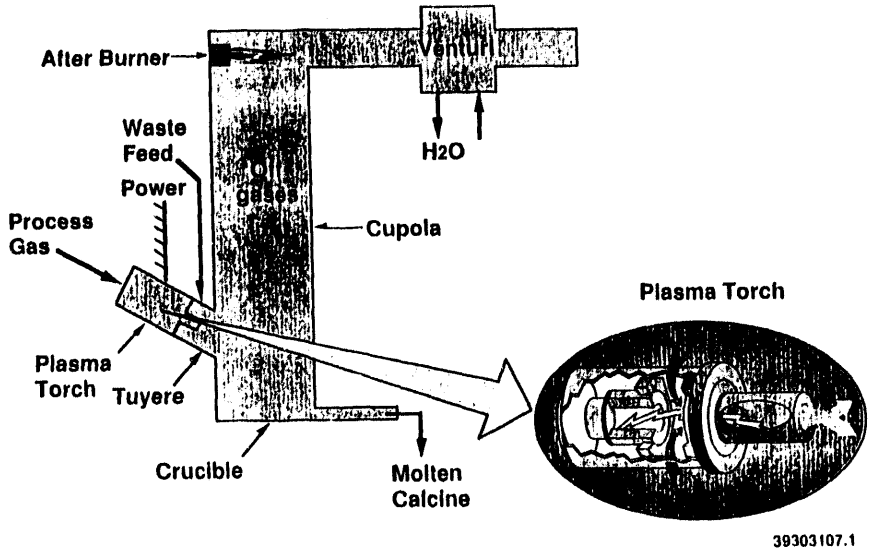

Figure 3. Calcination reactor system concept.

Activities supporting the FY 1993 testing will include detailed chemical analysis to better define the mass balances of the process and preparation of simulants for testing. Concurrent activities related to this project include chemistry development and residue leaching development. The chemistry development task will establish the current state of knowledge of the Hanford Site's tank wastes as it pertains to the chemical dynamics of the calcination and dissolution process steps. Laboratory testing will be used to verify and optimize process parameters and material balances. The residue leaching task will determine additional treatment techniques to further concentrate the TRU residue left from the calcination/dissolution process.

Biological Destruction of Tank Wastes

It is anticipated that existing biotechnology processes will be demonstrated as adaptable to DOE high-level and low-level liquid wastes stored in USTs. The approach that appears feasible is denitrification (reduction of nitrate to N_2) and simultaneous separation of the remaining radionuclide and heavy metal constituents of the waste by biosorption (adsorption into bacterial biomass).

The existing processes were initially evaluated for their applicability to the conditions and characteristics specific to buried waste at the INEL. Testing concluded that microbes were capable of denitrification under conditions of salt concentrations up to 4 Molar (sodium plus potassium) with acetic and phosphoric acids as the only added nutrients.

The approach for FY 1993 will identify how bioremediation can best be implemented within the process flowsheet currently proposed in the Hanford Site TWRS for pretreatment of tank waste. This will include

assessing tank waste characteristics, estimating potential impacts of anticipated "upstream" technologies, and identifying acceptable surrogate waste constituents. Further development will occur in the laboratory with operating a scale, continuous-flow bioreactor on simulated tank wastes (without metal contaminants) and assessing denitrification activity over a wide range of controllable conditions within the bounding conditions of the actual wastes.

Cesium Extraction Testing

This task will support development of the cesium extraction CPU for application to a variety of Hanford Tank Waste streams. The SRL, in coordination with Pacific Northwest Laboratory (PNL), will perform ion-exchange tests to obtain critical data needed for successfully designing and selecting the ion-exchange media for the CPU. Included in this task is the investigation of commercially available and foreign technology for cesium removal.

The SRL has developed a resorcinol-formaldehyde resin for cesium removal that has demonstrated superlative performance in testing at SRL, ORNL, and PNL. Other media for cesium removal either have much lower capacity or are incompatible with the high pH and aluminum concentration of Hanford and Savannah River Site wastes. The SRL will provide technical data, bench-scale tests, and technical consultation for cesium ion exchange and radiolytic stability of the resin in this task. Recent concerns with the resorcinol-formaldehyde resin regarding the potassium level in the waste will be investigated fully and resolved.

Nitrate to Ammonia and Ceramic Process

A patentable, inexpensive, and highly efficient method of decomposing the sodium nitrate component of tank wastes is being developed by ORNL. The supporting kinetic data for engineering use in pilot-scale design will be generated in bench-scale experiments followed by pilot-scale demonstrations. The process removes the sodium nitrate by reactions creating ammonia as a by-product. The remaining waste volume is converted to a solid, inert, ceramic-like product, with the sodium incorporated into the ceramic matrix. Significant waste volume reductions (65 to 70%) may be possible relative to processing with current methods (e.g., grout). Initial bench-scale tests have shown success, and a patent application is pending. Further bench-scale testing is planned for FY 1993 to allow selection of a reactor design. Engineering drawings are being prepared to support pilot plant construction and demonstration scheduled for FY 1994.

Tank Waste Processing Analysis

This task will evaluate pretreatment requirements of Hanford Site tank wastes on a tank-by-tank basis. Completion of this task will (1) identify the processing required for each tank to meet pretreatment criteria, (2) evaluate the effects of change in pretreatment criteria on processing requirements, and (3) optimize the deployment of distributed processes for pretreatment. Data from other DOE-funded associated tasks will be factored into this task, as indicated by the UST-ID and other programs.

COMPACT PROCESSING UNITS

The CPUs are self-contained units that will provide early deployment and testing of waste pretreatment technologies. Each CPU will contain a single phase of pretreatment (e.g., cesium extraction) and will be capable of deployment at or near the vicinity of the tank to be processed. The CPUs are capable of being used individually or in a series for potentially complete pretreatment of a waste stream. The CPU in-field deployment concept is shown in Fig. 4. The goal of CPUs is to facilitate treatment of selected tank waste within five years of program initiation using known technology and a phased addition of technology under development. The CPUs may be capable of being combined to meet the specific needs of each tank to be

remediated. Initiation of conceptual design on the CPUs has begun. Engineering evaluations have been initiated to place ion exchange for cesium extraction into the first CPU. Field tests are scheduled to begin operation in FY 1996. A CPU is a small relocatable process unit designed to treat tank waste at a rate of 2 to 5 gal/minute. This modular design concept will allow for offsite fabrication of the CPU components and reuse of the components for different process deployments. The principal design criteria for these components are discussed below.

Cesium Extraction Compact Processing Unit

A CPU for cesium ion exchange will be designed, built, and tested. Demonstration of the CPU concept is required before a decision to implement compact processing for the TWRS can be justified. The CPU for cesium ion exchange will address removal of cesium from Hanford Site tank waste supernatant. The PNL will develop conceptual design and a specification for the CPU and seek industry participation for detailed design and fabrication. The PNL will interact with SRL and industry to obtain ion-exchange data necessary to design this initial CPU for cesium ion exchange.

The current design concept is a single-pass regenerative ion-exchange concept using several columns, small feed tanks, and the associated piping, pumps, valves, and control systems. This process system will be enclosed in a containment structure providing shielding and containment adequate for installation and operation in the Hanford Site tank farms.

The development project began late FY 1992 and is progressing favorably. The major work breakdown elements are as follows: (1) Environmental Compliance, (2) Design, (3) Fabrication, (4) Component Testing and Installation, (5) Nonradioactive Demonstration, and (6) Radioactive Demonstration. The current design concept for the cesium extraction CPU is shown in Fig. 5.

Environmental Compliance and Permitting

These subtasks will prepare, submit for approval, and revise as required the documentation needed to receive the necessary approvals to conduct the CPU demonstration. The strategy for completing the associated environmental documentation is to proceed using a phased approach. The first phase will be preparation of environmental documentation to support the installation and nonradioactive testing for the CPU ion-exchange system. The second phase will be preparation of the documentation for the radioactive demonstration. This phased approach will allow the timely and cost-effective demonstration of the CPU concept.

Development activities up to and including the nonradioactive demonstration are not expected to require any permitting in addition to that currently in place at the Hanford Site. National Environmental Protection Act (NEPA) (2) documentation may be required. The radioactive demonstration is expected to require a NEPA Environmental Assessment, Resource Conservation and Recovery Act of 1976 (RCRA) (3) permit documentation, air permit documentation, and a safety analysis.

Design

The CPU will be designed as four major subsystems:

1. Ion-exchange process
2. Process controls
3. Enclosure/containment
4. Tank farm interface.

Compact Processing Unit

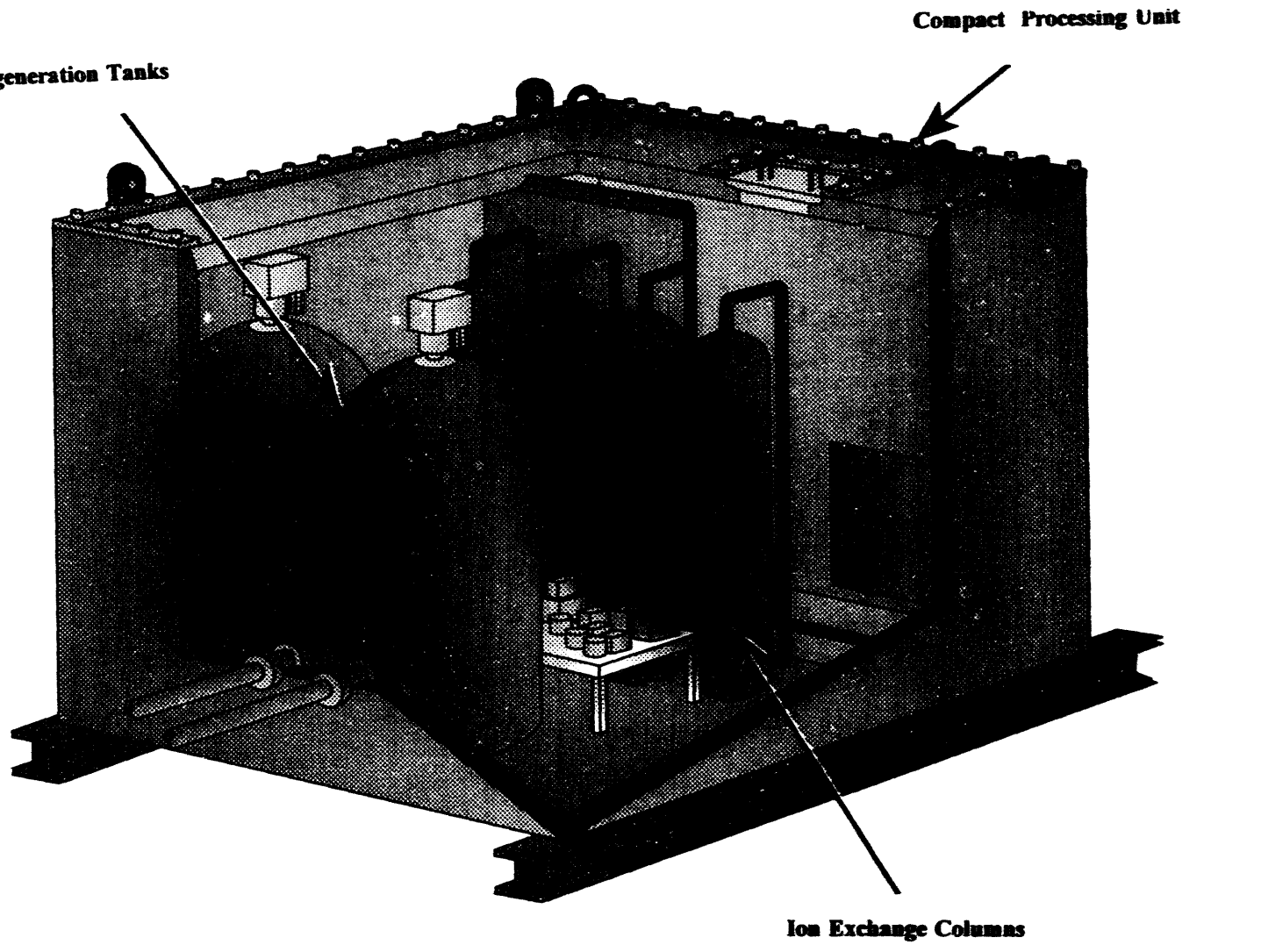

Figure 4. Compact processing unit deployment.

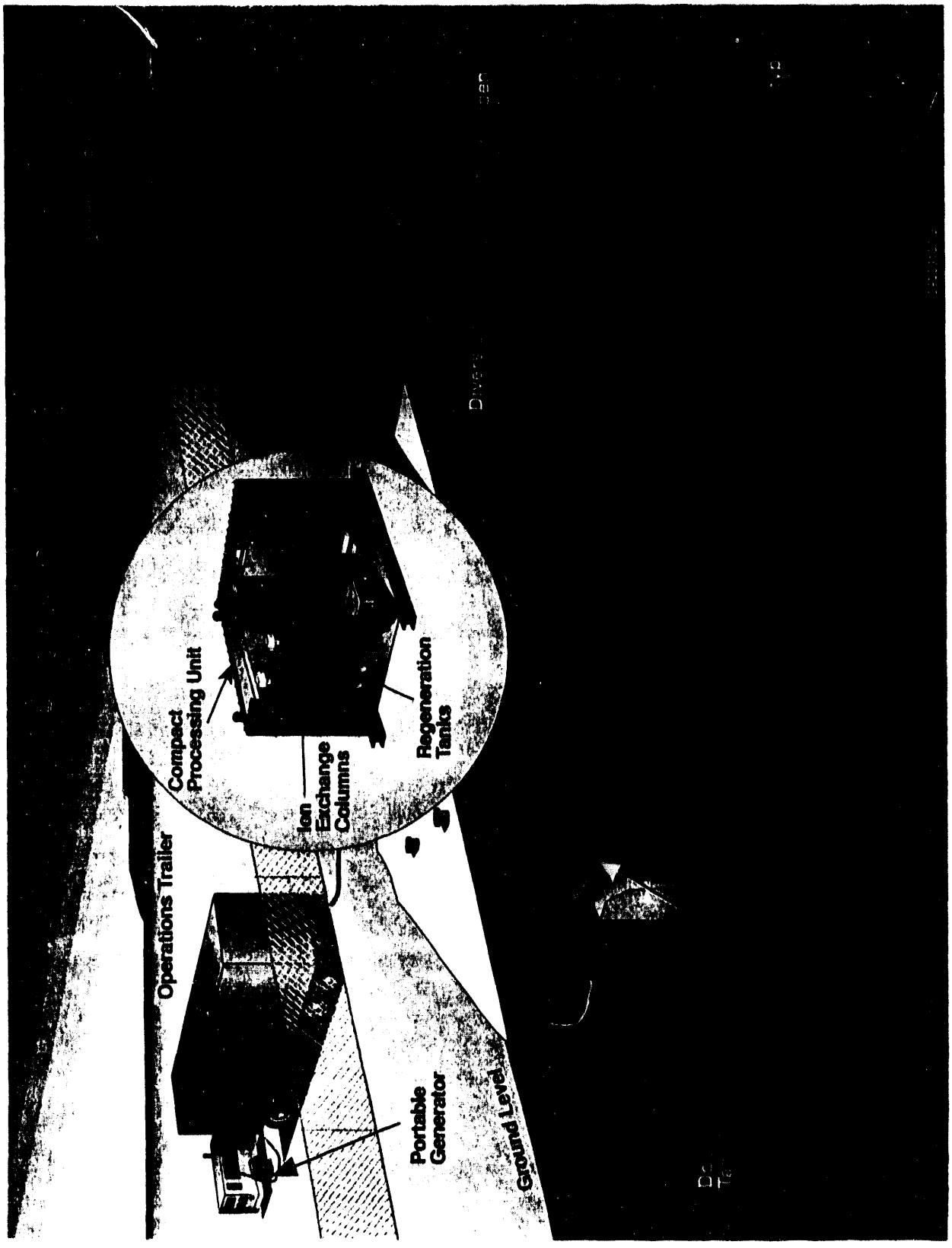

Figure 5. Compact processing unit.

Separation of the CPU design into these four subsystems has been done to facilitate phased completion and design focus when needed and allow a timely demonstration of the CPU concept. The ion-exchange process and controls will be designed and fabricated initially to support the nonradioactive demonstration. The enclosure/containment and tank farm interface will follow at a later time to support the radioactive demonstration.

Ion-Exchange Process Subsystem. The ion-exchange process system will be placed inside the containment enclosure and will interface with both the containment system and tank farm interface. The ion-exchange process system will provide for separating an incoming double-shell tank (DST) waste stream into a low-level cesium product stream and a concentrated cesium product stream and will have the capacity to remove cesium from 1,000,000 gal of Hanford Site DST waste (as stored) in one calendar year. The concentration of ^{137}Cs remaining in the waste stream will be less than the U.S. Nuclear Regulatory Commission (NRC) Class A limit of ≤ 1 Ci/m^3. In addition, the ion-exchange process system will adjust product streams to meet tank farm specifications and return the streams back to the tanks.

Process Control Subsystem. The process control system will be used to provide control and monitoring of systems associated with operation of the CPU. In addition, it will provide data acquisition and storage capabilities that will include a method for backing up data. The process control system will interface with the tank farm monitoring system.

Instrumentation and process control will be divided into two physically separated areas. One area includes the CPU enclosure, primary waste tank, chemical processing tanks, tanks for separated cesium, and any associated pumping and monitoring equipment or piping. The second area involves the Operator Control Station (OCS) where process control is initiated and monitored.

Enclosure/Containment Subsystem. The containment system will provide an enclosure for the ion-exchange process system. The enclosure, together with its heating, ventilating, and air conditioning (HVAC) and fire systems, will be designed to prevent the release of radioactive or other hazardous material to the environment and protect the public and personnel from exposure to radiation during process operations. The containment system also will provide an interface to the loading and transportation equipment that will be used to transport the CPU to the 200 Area tank farms.

Tank Farm Interface. The tank farm interface system will provide a suitable site for deployment of the CPU near a waste storage tank or diversion box in the Hanford Site waste transfer system. The bulk of the tank farm interface will be used to interface tank farm utility, waste transfer, and cold chemical supply systems to the CPU. Cold chemical makeup tanks and systems will be provided as part of the overall CPU system. In addition, the tank farm interface will include provision of standard utilities, including power, emergency power, potable water, and sanitary sewer to support CPU operations. Further, a mobile control room will contain the OCS. Where these utilities are not currently available, they will be provided by the CPU system.

The following primary design requirements for the CPU have been established:

1. Capacity to process 1,000,000 gal of Hanford Site DST waste in one year
2. Cesium decontamination factor of 10,000
3. Compliance with applicable DOE orders, RCRA, and Washington Administrative Code (WAC) 173-303 (4) regulations
4. Capable of operating acceptably and without significant maintenance for a minimum of one year
5. Design that permits relocation using a construction crane and a transport trailer. The availability of various transport trailers suitable for CPU transport will be investigated when a firm design estimate

of CPU weight and dimensions is available. (Design targets for an approximate overall CPU size of less than 15 ft by 15 ft by 15 ft and weight of less than 500 tons have been established to ensure that CPU transport is possible.)

Conceptual Design. Conceptual design activities are under way on this project, which began in September 1992. Accomplishments thus far include completion of functional and operational requirements, functional design criteria, and a predesign safety analysis. The goal is to establish the conceptual design by the end of FY 1993 and subsequently seek industry participation for detail design and fabrication.

Design Criteria. The CPU will be designed as a nonreactor nuclear facility to comply with the requirements for Radioactive Liquid Waste Facilities specified in DOE Order 6430.1A, "General Design Criteria" (GDC) (5), and WAC 173-303. The GDC references the necessary departmental orders, applicable federal laws, executive orders, and federal regulations as they specifically apply to each section of the order. A complete list of the regulatory requirements appears in Section 0106, "Regulatory Requirements." The following paragraphs highlight some of the detailed criteria of interest.

The CPU ion-exchange vessels and feed tanks will be designed and manufactured in accordance with the ASME Boiler and Pressure Vessel Code, Section VIII, Division I (6).

The CPU piping systems will be designed, fabricated, installed, inspected, and tested in accordance with requirements of ANSI B31.1-92, "Power Piping," (7) or ANSI B31.3-92, "Chemical Plant and Petroleum Refinery Piping," (8) as applicable.

The containment system for the CPU will be designed and fabricated to provide shielding, structural support, and containment suitable to support its use to transfer the contaminated process system to and from the in-field tank site to a maintenance and decontamination facility. This will invoke DOE onsite transportation requirements applicable to Type B quantities of radioactive material. In effect, this design goal will invoke some elements of the U.S. Department of Transportation (DOT) and NRC regulations for packaging and transport of radioactive material in the public domain (9,10). The extent to which the regulatory requirements are applied to the CPU design will be subject to DOE operations office review and approval.

Fire protection and detection systems will meet the requirements of National Fire Protection Association (NFPA) codes and standards. Further, fire protection systems will meet the requirements of DOE Order 5480.7, "Fire Protection" (11).

Detailed Design and Fabrication

Detailed design and fabrication of all of the CPU subsystems will be performed in a phased approach as noted for the overall effort. The ion-exchange and control subsystems will be first to be detailed and fabricated. Later, in a time frame to support the radioactive demonstration, the containment/enclosure and tank farm interface design and fabrication will be completed. The UST-ID Program plans to seek industry involvement in some of these efforts.

Component Testing and Installation

This subtask installs the CPU components for the various demonstration tests. Final assembly of the ion-exchange and process control subsystems will be performed to support the nonradioactive demonstration. Assembly of the complete CPU will be performed for in-field installation for the radioactive demonstration.

Nonradioactive Demonstration

A two-month nonradioactive demonstration of the CPU will be conducted using nonradioactive simulated wastes. This subtask will develop operating procedures for the CPU, train operating personnel, develop the test plan, conduct the demonstration using simulated tank waste (nonradioactive), and prepare a demonstration report. The operating procedures and practices used for this task will be developed to simulate radioactive operations as much as possible. This simulation will include constructing temporary walls to simulate the process enclosure and simulating various process equipment failures and recovery actions.

Radioactive Demonstration

The general objective of the radioactive demonstration will be to operate the CPU with actual tank waste within normal operational limits. A detailed test plan will be prepared and issued before testing. This subtask receives the system used for nonradioactive demonstration, performs any modifications required for radioactive demonstration, transports the CPU to the Hanford Site 200 Area, installs the CPU in the tank farm interface, and conducts a radioactive demonstration of the CPU for a period of one year.

Transportation. The CPU will be initially transported to the tank farm interface using a heavy-load transporter of suitable capacity. One system under consideration is the transporter currently used for moving decommissioned submarine reactor compartments from the Columbia River to burial grounds in the Hanford Site 200 Area. Upon completion of the demonstration, the CPU will need to be transported to an onsite facility for maintenance and/or decontamination. This transfer will be subject to DOE onsite transportation requirements. There is currently no expected need to ship a contaminated CPU or portions of one offsite. Such shipments, if they were to occur for any reason, would be subject to DOT and NRC transportation requirements.

Operation and Maintenance. The CPU will be deployed in the field for the radioactive demonstration. As such, TWRS will have operational responsibility, with the UST-ID Program remaining as the technical lead. The CPU is being designed to provide an operation interval of one year (in field) without the need for any maintenance. In-field operation activities will be performed remotely (i.e., from outside the containment) to minimize operator exposure. To ensure this demonstration objective, redundant components and routing flexibility through piping systems shall be used in high radiation areas, and readily replaceable components shall be used in other areas when a useful operating life of one year cannot reasonably be expected.

CONCLUSIONS

Nuclear materials production by the DOE and its predecessor agencies over the past fifty years has resulted in accumulation of large waste inventories and associated contamination problems. Included in the inventory is more than 100 Mgal of high-level and low-level radioactive mixed waste. The waste is currently stored in more than 300 USTs at five sites. The DOE has made a commitment to remediate the USTs and related near-field environments that are not in compliance with state and federal regulations and to treat and dispose of the wastes in accordance with currently accepted practice. However, the cost of cleanup of these tanks is prohibitive using some of the current baseline technologies. Furthermore, major gaps exist in key technology areas.

The UST-ID Program was created in February 1991 with a principal objective to develop and demonstrate technologies that will improve, accelerate, and reduce the cost and risk of this huge environmental remediation problem. The waste separations and pretreatment area of the UST-ID Program is developing a number of technologies with the potential to bring about significant improvements in the baseline approach. The basic approach is to bring promising technologies into the field and demonstrate their

performance while factoring the needs associated with multiple sites and types of waste. Balancing these needs presents one of the many challenges facing the UST-ID Program.

ACKNOWLEDGMENTS - The UST-ID Program is sponsored and funded by the DOE, Office of Technology Development. The funded projects are being conducted by several of DOE's operating contractors. The DOE-RL and WHC lead the program with Hanford as the host site. The CPU project is being conducted by PNL, with Mr. William G. Richmond as Principal Investigator.

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DECONTAMINATION FLOWSHEET DEVELOPMENT FOR A WASTE OIL CONTAINING MIXED RADIOACTIVE CONTAMINANTS

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ABSTRACT. The majority of waste oils contaminated with both radioactive and hazardous components are generated in nuclear power plant, research laboratory and uranium-refinery operations. The waste oils are complex, requiring a detailed examination of the waste management strategies and technology options. It may appear that incineration offers a total solution, but this may not be true in all cases. An alternative approach is to decontaminate the waste oils to very low contaminant levels, so that the treated oils can be reused, burned as fuel in boilers, or disposed of by commercial incineration.

This paper presents selected experimental data and evaluation results gathered during the development of a decontamination flowsheet for a specific waste oil stores at Chalk River Laboratories (CRL). The waste oil contains varying amounts of lube oils, grease, paint, water, particulates, sludge, light chloro- and fluoro-solvents, polychlorinated biphenyls (PCB), complexing chemicals, uranium, chromium, iron, arsenic and manganese. To achieve safe management of this radioactive and hazardous waste, several treatment and disposal methods were screened. Key experiments were performed at the laboratory-scale to confirm and select the most appropriate waste-management scheme based on technical, environmental and economic criteria. The waste-oil-decontamination flowsheet uses a combination of unit operations, including prefiltration, acid scrubbing, and aqueous- leachate treatment by precipitation, microfiltration, filter pressing and carbon adsorption. The decontaminated oil containing "de minimis" levels of contaminants will undergo chemical destruction of PCBs and final disposal by incineration. The recovered uranium will be recycled to a uranium milling process.

INTRODUCTION

Waste oils contaminated with radioactive and non-radioactive hazardous components are generated in nuclear power plants, uranium processing and research laboratory operations. Generally, waste oils consist of a variety of organic and inorganic components. Typical organic components include lube oils and machine oils, halocarbons, surface active and complexing agents, and paints. Inorganic components include water (light water, heavy water and tritiated water), acids, metals, and radionuclides. The primary radionuclides in the waste oil include ^{54}Mn, ^{60}Co, ^{134}Cs and ^{137}Cs. The common non-radioactive metals found in the oils include Pb, Cu, Fe, Ni, Mn and Cr.

Waste oils may also contain small amounts of suspended solids (inert as well as contaminant precipitates and colloids). In many situations, small amounts of water contained in the waste oils is present as a relatively stable emulsion.

Depending on the age of the oil, it is possible that some radioactive contaminant such as tritium could have exchanged with the hydrogen in the methylene groups contained in the oil. This is often termed "oil with

fixed radioactivity".

Waste oils appear to be sufficiently complex to require a detailed examination of the waste management strategies and technology options. Incineration of the waste oils (having fixed or non-fixed radioactivity) may offer a total solution. However, incineration may not be economically viable if only small quantities of waste oils are generated, or if waste oils generated at different locations have to be collected, blended and then incinerated in a central incinerator facility.

APPROACH TO WASTE OIL DECONTAMINATION

An alternative to incineration would be to decontaminate the waste oils to very low contaminant levels (e.g., some acceptable "de minimis" levels), so that they can be recycled and reused (if applicable), or burned as fuel in boilers (provided the total halocarbon levels of the decontaminated oils are below a certain value), or disposed of by off-site commercial incineration (requiring only hazardous waste registration).

Waste oils can be decontaminated by physical and chemical treatments. A variety of radioactive organic solvent cleaning methods available from different nuclear and non-nuclear industrial sectors can be applied to waste oil decontamination. The important features of any approach would include: 1) it is most appropriate for low-volume waste (e.g., a few thousand litres per month), 2) source treatment (waste oils are treated at their source), and 3) low capital and operating costs. However, if the major portion of the waste oil contained fixed radioactivity, then treatment processes based on the "usual" physical and chemical treatment methods may not work, in which case more vigorous decontamination methods would be required.

PREVIOUS STUDY

Reports by Electrical Powers Research Institute (EPRI) (1) and Siskind et al. (2) have summarized waste oil production and management at commercial power plants in the United States. At a recent CANDU Owners Group workshop [COG (3)], initiatives undertaken by Ontario Hydro for liquid waste management and some preliminary waste oil decontamination results were described.

Waste oils containing low levels of radioactivity are disposed of commonly by solidifying or absorbing them in any one of a variety of media, and subsequently burying them as low-level waste (Simiele et al.) (4). Other waste management techniques include incineration, and decontamination followed by incineration. Solidification requires that the waste oil be mixed with cement and/or other binder materials to approximately about one-half of the final waste-form volume. This increases the processing costs. Incineration is used at some plants in the United States. As suggested by Brewer and Fjeld (5), it is doubtful that incineration will be used at all plants. Presently, no incineration facility exists in Canada that can treat mixed radioactive waste oils.

Robertson (6) has proposed a method of decontaminating mixtures of radioactive water and water-immiscible organic liquids to produce a decontaminated organic liquid. The method consists of first separating the contaminated water and organic into two liquid fractions. The organic liquid is treated with a water-soluble chelating agent to remove substantially all radioactivity. The loaded aqueous phase and the contaminated water from the initial separation are decontaminated suitably.

From laboratory studies that used radioactive turbine oils from a boiling water reactor, (Simiele et al.) (4) have reported that over 95% of the total radioactivity has been removed by successive filtration, using 25.8 μm and 1 μm filters to remove particulates and centrifugation to remove water. The total activity of the waste oil was caused by ^{60}Co, ^{54}Mn and ^{137}Cs. They found that combining filtration and centrifugation with chemical washing with ethylene diamine tetra acetic acid (EDTA) was effective in producing a

decontamination factor (DF) in excess of 10 000 for ^{54}Mn and ^{137}Cs, but provided only a DF value of 1000 for ^{60}Co. In a subsequent study, Brewer and Fjeld [1991] have reported that oxidation of organic-phase binding of Cobalt-60 can be effectively employed as part of a waste oil decontamination scheme to provide high DFs for ^{60}Co.

EPRI (1) has proposed a conceptual process design and economic analysis for decontaminating lubrication waste oil containing free water, to remove radioactive cesium and cobalt. As free water is present, the cesium can exist as a molecularly dissolved species, while cobalt is assumed to exist attached to particulate. The process was designed to remove molecules and particulates from a two-phase system consisting of oil, water and some emulsions in either continuous phase. The main process steps consisted of adsorption and filtration. The filtration equipment consisted of 5 μm stainless steel filters, and adsorption of radioactive species was achieved by powdered solid sorbents; examples included a synthetic mordenite (particle size 5 to 12 μm) and a natural clinoptilolite. The final products from the oil decontamination process were water, oil and solid sorbent. It was suggested that the final product streams may be handled by several steps: 1) the product water containing some cesium can be processed through the power plant radwaste treatment system; 2) the treated oil may contain about 10 ppm water and is expected to have no detectable radioactivity; the oil may be reused or disposed of as a boiler fuel; 3) the used sorbent containing cesium, cobalt particles, water and oil may be mixed with an equal volume of dry sorbent, or calcined at 200 to 400°C in a muffle furnace with a slow air purge; the oil-free final mass is disposed of as low-level waste, or calcined at 1000 to 1200°C, to produce a solid glassy material and then disposed of as low-level waste.

Krasnai et al. (3) have reported a preliminary study using a waste oil from a CANDU power reactor in Ontario, with the objective of decontaminating the oil for reuse or for on-site disposal. The oil decontamination criteria included: a) reduce tritium concentrations to less than 2 μCi/L, b) reduce beta and gamma activity to the detection limit (about 3.7×10^{-4} μCi/L) at the generating stations, c) reduce lead and cadmium concentrations to less than 5 mg/kg and 0.5 mg/kg, respectively, and d) produce only solid secondary wastes from the decontamination process, while avoiding the generation of secondary liquid wastes. From scoping bench-scale tests, they have suggested a combination of unit operations, including filtration, vacuum gassing, MgO/SiO^2 adsorption and acid scrubbing as potential components for the specific waste oil decontamination.

URANIUM WASTE-OIL MANAGEMENT STRATEGY FOR IMPLEMENTATION AT CRL

A mixed waste oil stored in 582 drums at Chalk River Laboratories (CRL), AECL Research, Ontario is being considered for treatment and disposal. The bulk of the waste oil consists of lube oils, paints, solvents, and some water and sludge. The waste oil is stored in two groups: 1) non-PCB (waste oils, and 2) PCB-containing waste oils (63 drums). The only radioactive contaminant in the non-PCB and PCB waste oils is uranium, present as natural and depleted uranium. In the case of PCB oils, the primary contaminants are uranium and PCBs. In addition to the two contaminants, the waste-oil drums contain different amounts of halocarbons (primarily chloro-organic solvents, such as trichloroethylene and methylene chloride, and to a lesser extent fluorocarbons). The total quantity of non-PCB oils is about 100 000 litres and for PCB oils it is about 10 000 litres.

It is apparent that once the uranium concentration in the waste oil is reduced to a "de minimis" level, the treated oil can be disposed of readily. Non-PCB treated oils can be disposed of by off-site shipment and incineration. The treated PCB oils can be chemically detoxified by a licensed sodium process available in Ontario, and the resulting non-hazardous oils can be recycled or incinerated; the sodium chloride sludge generated can be disposed of in an approved landfill. The uranium recovered from the waste-oil treatment can be converted by precipitation to "yellow cake", and can be recycled into a uranium milling circuit in Saskatchewan, Canada.

EXPERIMENTAL

Waste-Oil Characterization

The waste-oil inventory was determined by weighing individually all 582 drums. The waste-oil samples from individual drums were grouped into composites of ten, for chemical analysis. The choice of the samples that went into each composite was based on the physical appearance and the suspected presence of PCBs. All the samples were analyzed for total halides, uranium and PCBs. Where there was some uncertainty, the composites were split into individual samples or smaller composites, to determine the distribution of concentrations within the composite.

Chemical analysis for uranium, PCBs and total halocarbons was performed using composite waste-oil samples, and in some instances by individual drum samples. A Dohrman TOX-20A Analyzer was used to determine total halides in oil samples. A gas chromatography with capillary column and an electron capture detector was used to analyze for PCBs. The detection limit for PCBs by gas chromatography is 1 ppm for oil. The detection limit for total halides varies, depending on the sample and how much it is diluted. The variation usually lies in the range of 10 ppb to 1 ppm.

Uranium content of the oils was measured by first digesting the oil in concentrated nitric acid and analyzing the aqueous sample fused with sodium fluoride fluorometrically. For scrubbed oil leachate solutions in process development tests, samples were also analyzed by ICP. The detection limit for uranium was less than 0.038 mg/L.

Waste-oil drums were counted for extended periods, to ensure that there were no other radioactive species such as tritium, cesium-137, etc., present in the oil.

Selected composite oil samples were finger-printed using GC-MS.

A series of experiments were performed to determine other related metal contaminants in the waste oil. Non-PCB oil samples taken from a composite formulated by mixing individual drum samples of non-PCB and PCB waste oils were subjected to an extended concentrated nitric acid digestion procedure. The aqueous extract obtained from the digestion was analyzed.

Bench-Scale Waste-Oil Decontamination and Metal Recovery

Waste-oil scrubbing tests were conducted in temperature-controlled glass vessels (1 L to 5 L volume) equipped with mechanical agitators. Separation of the oil-water mixture was carried out either by prolonged gravity settling in separatory funnels or by centrifugation, as required. The acidic extracts containing uranium and other metals were subjected to precipitation by adding ammonia or magnesium hydroxide in stirred glass vessels. The low- concentration suspension was filtered at about 15 psi through flat-sheet polypropylene microfilter (0.2 μm pore diameter) contained in membrane cells purchased from Amicon Corporation. Organic carbon was removed by directly adding activated carbon to the solution to be treated, or by using a column packed with an activated carbon. The Total Organic Carbon (TOC) was analyzed using a Dohrman Carbon Analyzer.

RESULTS AND DISCUSSION

The average concentration of major compound groups and total inventory is summarized in Table 1. The typical concentration of metals in non-PCB oils is given in Table 2. The data illustrate that although the amounts of the toxic contaminants are relatively low, they can not be ignored in formulating a waste management strategy for the waste oils. Key volatile organic compounds and extractables are summarized

in Tables 3 and 4, respectively. Base neutrals extractables (EPA 625) were all below the minimum detection limit.

Table 1. Average concentration and inventory of Uranium, PCBs and total halocarbons in non-PCB and PCB oils.

Compound	Non-PCB Oil			PCB Oil		
	Uranium	Halocarbon	PCBs	Uranium	Halocarbon	PCBs
Total No. of Drums		519			63	
Oil Density (kg/L)		0.845			0.845	
Total Oil Weight (kg)		88,000			9,250	
Av. Conc. (ppm)	5,390	33,180	10	1,150	3,200	1,150
Compound Inventory (kg)	490	2,950	1.23	10.6	29.6	10.6

Table 2. Typical composition of selected metals in non-PCB waste-oil composite samples.

	[Ba]	[Fe]	[Cu]	[Pb]	[Ni]	[Zn]	[As]	[Cr]	[Cd]	[U]
Concentration (mg/Kg)	13	557	43	84	110	224	<4	12	<1	4430

Table 3. Typical volatiles in the waste-oil composite

Compound	Average Concentration (mg/kg)
Benzene	8
Bromodichloromethane	76
Chloroform	218
1,1-Dichloroethane	106
Ethylbenzene	2 540
Methylene chloride	6
Tetrachloroethane	728
Toluene	10 600
1,1,1-Trichloroethane	5 160
1,1,2-Trichloroethane	398
Trichloroethene	10 800
m.p.-Xylene	11 900
o-Xylene	12 100

Table 4. Typical extractable organics.

Compound	Concentration (mg/kg)
1-ethyl-2-methyl-benzene	15 100
1,2,3-Trimethylbenzene	27 500
2-ethyl-1,4-dimethylbenzene	12 600
1,2,3,4-tetramethylbenzene	11 500
1-ethyl-3,5-dimethylbenzene	12 900
1,3-dimethylpyrene	11 900
4-phenyl-bicyclohexyl	23 400
9-methylnonadecane	4 900
tetratetracontane	2 900
pentatriacontane	4 500
hexadecane	5 200

Waste-Oil Scrubbing to Remove Uranium and Other Metals

Of the series of experiments performed using composite samples of the waste oils (PCB oils and non-PCB oils), test results have shown (Table 5) that scrubbing the waste oil with an equal volume of 1 mol/L sulphuric acid at about 50 to 55°C provides the best decontamination for removing uranium originally present in the waste oil. Depending on the target level of uranium in the treated oil, a combination of multi-stage scrubbing, or single-stage scrubbing with long contact times (of the order of 24 hours) between the acid and the waste oil is required. By optimizing the operating variables, it appears that the uranium concentration of the scrubbed oil can be reduced to less than 10 ppm. The actual concentration of uranium varies with the number of scrubbing stages and/or the contact time.

In addition to removing uranium, acid scrubbing removes most other metals present in the oil. The high concentrations of certain metals, including iron, zinc and nickel, are the result of corrosion of oil drums due to long storage. The presence of low-concentration metals has been attributed to metal particulates introduced when using the original clean oil in machine lubrication.

During the scrubbing experiments it was observed that a small amount of organics were lost to the acid phase containing uranium, due to organic solubility in water and/or a physical entrainment during the oil/water separation step. The measured TOC in the separated acid phase varied in the range of a few hundred ppm to a few thousand ppm. In pilot- or engineering- scale operations, the organic carry-over by entrainment can be virtually eliminated. Nevertheless, a certain amount of soluble organics, primarily originating from the dissolution of low-chain solvents such as methylenechloride and trichloroethylene, is bound to be present in the acid extract phase.

Removal of Uranium and Other Metals from Acid Solution

The dissolved and precipitated metals from the acid extract were subjected to precipitation at alkaline conditions (pH ~ 10) using ammonium hydroxide. The precipitation reagent was selected primarily to produce a uranium product, 'yellow cake', compatible for reuse in a specific uranium milling circuit. Other reagents, such as magnesium hydroxide, are equally suitable. Alkaline precipitation was found to have beneficial effects: a) iron precipitates scavenge a number of dissolved metal ions; and b) small amounts of arsenic are co-precipitated with iron. After precipitation, the dilute suspension was filtered through a microfiltration membrane and the filtrate was analyzed. Results given in Table 6 illustrate that virtually most metals can be effectively removed by the process, and the final filtrate can be discharged after a TOC removal step.

Table 5. Selected Waste-oil decontamination results.

Waste-oil scrubbing condition	Oil to scrub ratio	No. of stages	Temp. (°C)	Uranium conc. in oil (ppm)	
				Initial	Treated oil
Non-PCB Oil:					
Scrubbing a composite sample of 1.5 L from 519 waste-oil drums with 1 mol/L H_2SO_4 for 8 h per stage	1:1	3	55	4 820	<10
Scrubbing a composite sample of 200 mL from 249 waste-oil drums with 1 mol/L H_2SO_4 for 15 min per stage	1:1	3	50	12 250	7.5 to 14.4
Scrubbing a composite sample of 200 mL from 249 waste-oil drums with 0.05 mol/L *Ionquest 201 for 15 min per stage	1:1	3	23	12 250	7.9
* Ionquest is a thermally unstable complexing agent from Albright & Wilson Americas					
PCB Oil:					
Scrubbing a composite sample of 1.5 L from 63 waste-oil drums with 1 mol/L H_2SO_4 for 8 h per stage	1:1	2	55	778	2.7
Scrubbing a composite sample of 200 mL from six waste-oil drums ([PCBs] = 1146 ppm; [total halides] = 1355 ppm) for 15 min per stage with:	1:1	2	55	778	2.7
(a) 1 mol/L HNO_3	1:1	5	24	1200	26.0
(b) 1 mol/L H_2SO_4	1:1	5	24	1200	38.8
(c) 1 mol/L H_2SO_4	1:1	5	55	1200	3.0
(d) 1 mol/L H_2SO_4 (24 h)	1:1	1	24	1200	22.8

TOC Removal from Metal-Depleted Filtrate

In the sulphuric acid scrubbing of waste oil at room temperature, with an oil water ratio of 1:1, an average of about 300 ppm TOC per scrubbing stage was found in the acid extract. The TOC levels increase sharply to an average value of 1450 ppm when the oil scrubbing was performed at 55°C. Although the presence of TOC (100 to 2000 ppm) did not adversely influence metal precipitation efficiency, it should be reduced

to less than 15 ppm, so that the bulk water stream can be discharged.

Preliminary TOC removal tests were performed using powdered activated carbon in solution (0.2 gram activated carbon per litre water) combined with filtration and single-pass of water through a 2.5-cm dia. x 15-cm deep fixed-bed column. The treated water after carbon adsorption showed that the TOC levels can be easily reduced to less than 5 ppm in the final discharge water.

Table 6. Typical metal removal efficiencies and metal concentrations in the final effluent produced by precipitation-microfiltration using the acid extract of the non-PCB waste-oil composites.

	As	Cr	Fe	Mn	U
Initial Conc. (mg/L)	0.26	1.0	97.5	1.0	813
Removal Efficiency (%)	98.9	97	99	70	>>99
Filtrate (effluent) Quality (μg/L)	3	30	700	300	<38

Table 7. Characteristics of a Composite Sample of non-PCB Treated Oil Evaluated for Disposal by Incineration

Characteristic Tests	Organic	Aqueous	Sludge/ Emulsion	Overall
Phase separation (%v/v) on standing for 1 h	100%	--	--	
Phase separation (%v/v) centrifuged for 5 min	80%	10%	10	
Density (kg/L)				0.948
Heat value (MJ/kg) @750°C				24.8
Total ash (%w/w)				5.4
Kinematic viscosity @25°C (cS)				<100
Flash point (Closed Cup °C)				>61
Total halogen (%w/w)				0.33
Organic halogen (%w/w)				0.33
PCBs				N/D

Desired Characteristics for cost-effective disposal by incineration:
- Heat value - 30 MJ/kg (minimum)
- Ash content - 10% (w/w) maximum
- Viscosity - less than 500 cP

Treatability Tests for Incineration Using Composite Samples of Uranium-Depleted non-PCB Oils

Uranium-depleted non-PCB oil samples obtained from bench-scale acid scrubbing tests were tested off-site at a commercial laboratory, to determine the suitability of treated oils for incineration and to obtain disposal costs (7). An example of treated oil characteristics is given in Table 7. The results have shown that the treated oil is suitable for incineration.

Detoxification of Uranium-Depleted PCB Oils

Samples of uranium-depleted PCB oils (average concentration of PCBs ~1146 ppm) were chemically detoxified off-site using a licensed process available commercially. This mobile technology utilizes sodium metal to remove chlorine atoms from the PCBs, thus making the oil non-hazardous. The final non-hazardous oil after PCB detoxification can be disposed of by incineration similar to treated non-PCB oils. Initial treatability tests conducted by a commercial vendor (8) using uranium depleted oil samples have shown that the PCBs can be adequately detoxified.

DETERMINATION OF DE MINIMIS LEVEL FOR URANIUM IN TREATED OIL

The oil may qualify for a "de minimis" waste designation once the uranium level in the oil waste is reduced to an approximate concentration of 10 ppm. A "de minimis" dose represents a level of risk that is generally accepted as being of no significance to an individual, or in the case of a population, of no significance to society. This level is derived from a small fraction of the annual dose due to natural background radiation, and represents an extrapolation from a fatality risk of 10^{-6} from cancer [AECB, 1989]. In the province of Ontario, the individual dose from all natural sources is generally 3 mSv/yr (9).

The Atomic Energy Control Board (AECB) Regulatory Document [AECB, 1987] states that a "de minimis" individual dose limit for radioactive waste disposal is 50 μSv/a, provided that the radiological impact will be localized and the potential for exposure of large populations is small. Below this dose criteria, regulatory limits are not required. However, the Advisory Committee on Radiological Protection (ACRP) and the Advisory Committee on Nuclear Safety have recommended a "de minimis" individual rate of 10 μSv/a, and a "de minimis" collective dose rate of 1 person-Sv/a (10).

The radiological impact of transporting treated non-PCB oil (100 000 L) -- having an arbitrary uranium level of 10 ppm -- from the CRL site to a commercial incineration facility in Ontario, and performing incineration and subsequently disposing of the incinerator ash in a secure landfill, was analyzed. The analysis was performed using IMPACTS-BRC Version 2, a generic radiological assessment computer program developed by the U.S. Nuclear Regulatory Commission to classify certain waste streams as below regulatory concern (11). Radiological impacts (doses) were estimated for several pathways, including direct gamma-radiation exposure, worker inhalation and exposure, off-site atmospheric and water releases, and intruder exposures. Annual impacts were evaluated for a variety of individuals and population groups. The impacts were grouped under: (i) transportation related, (ii) disposal operation related, and (iii) post-disposal related.

The impact analysis results have shown that:

- The individual and population doses in each pathway are linearly proportional to the uranium concentration in the treated oil.
- The individual doses both from the short- and long-term impacts of incineration/disposal of treated oils still having 10 ppm of natural uranium are minimal; a member of the public may receive 0.003 μSv from incineration operation and an insignificant dose from the day-to-day operation of the disposal site; a disposal site worker may receive about 0.2 μSv/a from working

at the incinerator and about 0.2 μSv/a from working at the disposal site.

- The long-term impacts from the groundwater contamination are found to be minimal; for example, after 2000 years, an intruder may receive 0.002 μSv from consuming and using water from a well driven into the ground at the periphery of a disposal site.
- The maximum dose to an individual is associated almost exclusively with the waste transportation pathway. As a result, the individual dose to a transportation worker can be used to estimate the maximum activity level in the treated oil that corresponds to the "de minimis" dose criteria of 50 μSv/a; For 10 ppm uranium, the maximum individual dose associated with the transportation pathway is calculated to be 4 μSv/a.
- To meet the 50 μSv /a "de minimis" dose criteria, an approximate estimation shows that a maximum concentration of natural uranium up to 125 ppm may be allowed in the treated oil. For the more restrictive ACRP recommendation of 10 μSv/a, the uranium concentration in the treated oil should not exceed 25 ppm.

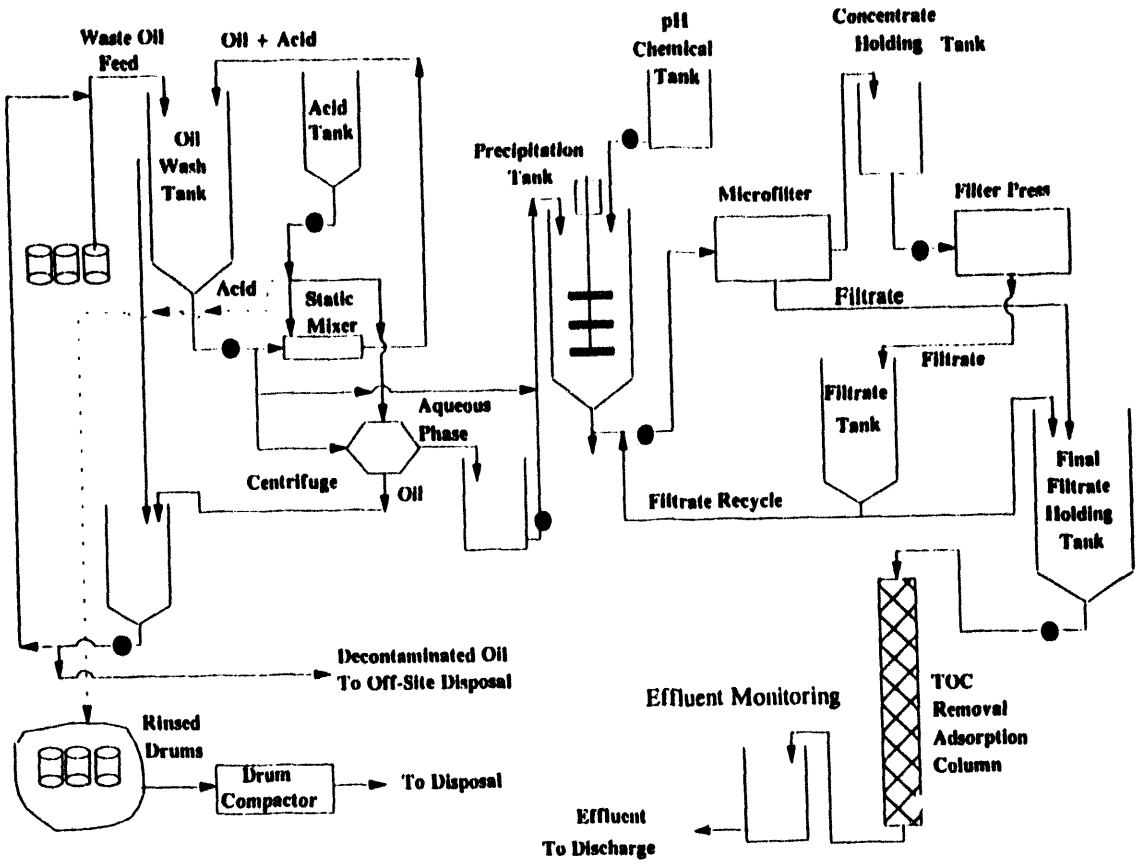

Figure 1. Flowsheet for Waste Oil Decontamination/Disposal

PROCESS FLOWSHEET

A waste-oil decontamination flowsheet was designed using 1 mol/L sulphuric acid as a scrubbing solution. As the uranium concentration in each waste oil drum varied appreciably (about 10 ppm to 20 000 ppm U), to maintain flexibility in the treatment it was decided to perform the acid scrubbing portion of the flowsheet as a batch-wise operation.

The overall process scheme is schematically shown in Fig. 1. The principal process steps are summarized below. The flowsheet is applicable to non-PCB as well as PCB waste oils. The portion of the flowsheet to remove and concentrate metal contaminants from the scrubbed acidic solution is based on the groundwater treatment technology developed by AECL for mixed radioactive contaminants through a cooperative program between AECL and the U.S. Department of Energy (DOE), managed through Argonne National Laboratory (12).

The oil-decontamination process involves three major steps: (i) waste-oil scrubbing with sulphuric acid, to remove uranium and other metals; (ii) precipitation and concentration of uranium and other metals from scrubbed acidic solution; and (iii) removal of TOC by activated carbon polishing columns.

Based on the results obtained from bench-scale tests, the oil-scrubbing step, using 1 mol/L sulphuric acid and sufficient contact time (several hours), can be performed in batches of 2500 to 5000 litres of oil using large tanks, with gentle agitation and a closed-loop recirculation of the tank contents through a static mixer system. In this step, the waste oils will be scrubbed with about equal volumes of acid at about 50-55°C in large fiberglass-lined tanks, until the treated oil reaches a uranium concentration value of less than 10 ppm. The treated non-PCB oil will be shipped off-site for incineration and landfill disposal.

In the second step, the uranium bearing acidic aqueous extract, containing small amounts of dissolved and suspended organics, will be precipitated using hydroxides of magnesium or ammonia. The chemistry of uranium precipitation is such that almost complete precipitation/co-precipitation/ion scavenging of uranium, along with other metals (Fe, Pb, Zn, As, etc.), will be achieved around pH values of 7 to 8. Once precipitated, the dilute suspension containing metal precipitate can be concentrated by a factor of 20 using cross-flow microfiltration. The uranium suspension at around 2 to 5% (w/w) can be further concentrated in a filter press essentially, to a wet cake (about 30% dry weight) (13). The precipitated uranium, along with other metals, is packaged in drums and shipped to a uranium processing complex, for reuse by adding to the uranium milling circuit.

Based on bench-scale test results, the bulk of the water stream (filtrate) resulting from the precipitation-concentration operation is expected to contain only trace amounts of metals at the ppb level. This stream will be monitored for uranium and TOC, and as needed will be sent to the polishing process.

As required, a series of two activated carbon polishing columns will be used in the second step, to remove residual metals (if any) and TOC from the bulk water stream. Once the water stream from the polishing unit fully meets the target discharge limits, it can be discharged to the site aqueous effluent system.

The estimated amount of aqueous solutions generated during the entire processing period is expected to be between 250 000 and 300 000 L.

The unusable/exhausted carbon will be shipped off-site for incineration/disposal, as needed.

The final waste-management component is to ensure that the empty waste-oil drums are conditioned and compacted adequately before disposal. As required, the residual oils remaining in the drums are flushed with a combination of a dilute sulphuric acid solution and/or limited amounts of varsol. Special care will be exercised to clean thoroughly the residuals in the empty PCB drums. The clean drums are to be compacted using a mechanical compactor and disposed of at the CRL site.

CONCLUSIONS

- As the mixed oil waste contains only natural and depleted uranium, the removal of uranium to produce a clean oil is a viable waste-management option.

- By properly choosing the operating variables, we have shown that a decontaminated oil containing uranium concentrations less than the targeted "de minimis" level of 10 ppm uranium can be readily accomplished and quality assured.
- A simplified version of the AECL-US DOE groundwater treatment technology is adequate to recover uranium and other metals from acidic extracts.
- The dissolution of some of the organic species (light organics and surfactants) in the aqueous extract phase (~3 to 4 %) makes it essential to incorporate a TOC control process step before the uranium-depleted aqueous effluent can be safely discharged.
- The recovered uranium product (yellow cake) can be recycled into a uranium milling process.
- The radiation dose from incineration/landfill disposal of the treated non-PCB oils still containing 10 ppm of natural and depleted uranium does not appear to be a significant health risk to workers or to the public, and is well below the 50 μSv/a "de minimis" limit, in accordance with the AECB criteria for disposal. The maximum individual dose is found to be associated with the transportation pathway, and is calculated to be 4 μSv/a for oil containing 10 ppm uranium.
- Development and analysis with non-PCB uranium waste oils shows that management of the oil through uranium decontamination to a "de minimis" level of 10 ppm and disposal of the treated oil by off-site incineration is an attractive strategy for safe and cost-effective implementation.
- The uranium in PCB waste oils can be decontaminated in a manner similar to non-PCB oils, except that the PCB-containing treated oil is chemically detoxified and then disposed of by incineration.
- The required facility for the selected waste-management option is being assembled. The current plan is to treat and dispose of the majority of the non-PCB waste oils (~ 100 000 L) by the end of 1993.

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CHAPTER 3

Regulatory Issues: General Topics

MIXED WASTE: BEFORE TREATMENT, STORAGE AND DISPOSAL

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ABSTRACT. If we are to address the problems associated with mixed waste, those responsible for it must understand and take into account not only the regulatory context and technical information, but also public concerns. They must do so at the earliest stages of developing potential solutions to the licensing/permitting, handling, treating, storing, and disposing of mixed waste. This demand places a premium on approaches that promote the participation of all the diverse segments of the public in decision-making about mixed waste issues.

The management of containerized and low level mixed wastes is a problem at many locations within the Department of Energy (DOE) Complex. Satisfactory characterization, treatment, and/or disposal of the contents of these containers involve diverse technical, regulatory, public health, and safety issues. Opening containers to determine their waste presents potential health and safety threats to the immediate workers and the surrounding population. Technologies and techniques for non-intrusive analysis are not readily available. Further, characterization requirements could vary significantly depending upon the treatment and disposal options selected. Decisions on characterization and treatment/disposal are directly driven by regulatory requirements (including the requirements of the disposal sites chosen), treatment parameters, the ultimate disposal site, transportation routes, and, it should go without saying, public acceptability.

When public participation and regulatory factors are considered in the earliest stages of the decision-making process, especially prior to and during technology selection, public understanding and regulatory confidence increase. This in turn should foster more efficient, cost effective approaches to DOE's mixed waste problems in which regulatory delays are minimized and costly legal challenges are less likely. This paper describes the Center's work in assisting DOE to find effective ways of incorporating public and regulatory input into the planning process surrounding containerized low level mixed waste.

FOCUS

If we are to address the problems associated with mixed waste effectively, those responsible for it must understand and take into account not only the regulatory context and technical information, but also public concerns. They must do so at the earliest stages of developing potential solutions to the licensing/permitting, handling, treating, storing, and disposing of mixed waste. This demand places a premium on approaches that promote the participation of all the diverse segments of the public in decision-making about mixed waste issues. This paper explores the efforts of the Colorado Center for Environmental Management (CCEM) to help Department of Energy (DOE) and states with DOE facilities to find mutually acceptable and effective ways of dealing with mixed waste.

BACKGROUND

The Center was created in March 1991 in response to an initiative of Colorado Governor Roy Romer. It brings together a unique mix of companies, citizen and environmental groups, nonprofit organizations, government agencies and educational institutions in a broad-based cooperative endeavor to address environmental issues in Colorado and the United States.

In July, 1991, the DOE awarded a five-year grant to the Center to support the Technology/Regulatory Integration Project (TRIP). This grant enables the Center to focus attention on the public participation and regulatory dimensions of waste management and environmental restoration.

CCEM has undertaken the TRIP Project to develop and assess alternative ways for achieving effective citizen participation and timely regulatory review in decision-making in environmental restoration. TRIP's particular focus is to find better ways of incorporating public input and insuring timely regulatory review into the selection and deployment of innovative technologies for characterizing, remediating and restoring hazardous waste sites, *without increasing risks to the surrounding community and environment.*

As part of TRIP, the Center is creating a forum where all stakeholders can address and share their specific concerns associated with mixed waste. The Center has assembled a diverse group, including citizens' groups, environmental organizations, state and Federal regulators, local and state government officials, DOE headquarters and field staff. This group is working to develop the best approaches for characterization, treatment and disposal of containerized mixed wastes with a particular focus of consensus-building.

The TRIP project began with the realization that the environmental restoration process is a detailed and elaborate combination of government regulation, public participation, and scientific and technological issues. The complex interaction of these components is often inconsistent and at cross purposes, and, in the absence of any mechanism to integrate conflicting goals and expects, frequently promotes poor decision-making.

INITIAL EFFORTS

During 1991-1992 (Phase I) TRIP focused on:

- identifying a series of "critical success factors" or principles for effective public involvement, and
- laying the foundation for projects to demonstrate and test these principles.

We organized a series of town meetings held throughout Colorado. These were designed to give the public a chance to voice their concerns about environmental issues as well as to solicit public input into the design of the TRIP project.

Networking With the Diverse Publics Concerned with Hazardous Waste Issues

TRIP did a series of interviews with groups and entities actively involved in or concerned with environmental restoration. We talked with federal agencies including the General Accounting Office (GAO), the Environmental Protection Agency (EPA), Department of Defense (DOD), and Department of Interior (DOI). We met with representatives of national environmental groups, think tanks, and state and local government officials. All told, TRIP surveyed more than 900 people throughout the United States. With this information, we designed a list of focused issues, which are the variables that define how well DOE—or any other public or private agency doing a cleanup project—implements new

technologies. These are issues that are not being addressed fully by other entities and that offer the potential for more effectively integrating public participation and regulatory review into the process. Conducting Case Studies of key Hazardous Waste Cleanups Across the CountryThese sites were chosen to give those concerned with the issues surrounding environmental restoration a sense of how publication participation and regulatory factors have affected the course of cleanup in a variety of settings and under a number of different regulatory "drivers."

Developing the Necessary Communication Tools

Through various workshops, CCEM tested and refined communication tools and outreach strategies to integrate public participation. The Center also established information delivery systems, including a quarterly newsletter, environmental directories, and an electronic bulletin board. The newsletter forms the basis of our ongoing communications with the public. Our bulletin board extends the access to environmental information. It contains a calendar of events, the capacity for electronic mail, meeting minutes, and environmental databases. The directories publish information of general use to the public. For example, The Colorado Environmental Resource Directory lists the environmental firms operating in the state and the goods and services they produce. Note that this is a public assess bulletin board, operating continuously (except for brief periods of maintenance), using the telelphone no. (303) 232-8541.

PHASE I: FINDINGS

Phase I findings focus on the principles of effective public participation in decision-making. They reflect the case studies, CCEM's public meetings and workshops, and extensive interviews with experts in the environmental field. We've made every effort to represent the broad range of viewpoints typical of environmental issues and characteristic of the Center.

We've distilled a set of principles of effective public involvement. Many of these seem obvious on reflection. They are, however, honored more in the breach than the keeping. These "lessons learned" form the basis and framework for developing and implementing an integrated approach to environmental management.

Early and Consistent Public Involvement

Early, consistent involvement of the regulators and the public is not required under current cleanup processes. While frequently identified as a key to successful public involvement, it is rarely practiced. The public needs to be part of the decision-making process from start to finish, not just during the public comment periods stipulated by law.

Community Concerns

Identify community concerns early and thoroughly. Successful public involvement demands an understanding of what the important issues are for a given community and site and requires we identify the "deal breakers" that can stop a project if not dealt with early on.

Honesty

This is a very simple point, but it bears repeating: honesty is the best policy. That means being clear about what is or isn't known. The public needs to have the best information and to understand the limits of scientific knowledge and certainty.

Authority and Empowerment

"Empowerment" has become as much of a catch phrase as "proactive." No one will argue against empowering citizens. Any real world situation, however, is more complicated than these buzz words convey. Decision-making authority is frequently a matter of legislation and regulation. It's important to be clear about what type of participation and control of the decision-making process citizens have. Public involvement efforts can create false expectations when authority and roles are not clearly established from the outset.

Risk Analysis

Some of the most contentious environmental issues relate to risk and risk assessment. Too often, the public is not involved in the risk assessment process; they are given a package of information after the analysis is done. The implication is: trust the experts; this is good science. Such an approach is simply not acceptable to the public who need to be a part of the process in order to "buy-in" to the conclusions reached.

Experts and the Public

Having technical personnel, rather than only community relations staff, talk to the public builds credibility. To be effective in this role technical staff and managers need some rudimentary training in community relations and effective communication. This doesn't eliminate the need for trained and skilled community relations support—it enhances the effectiveness of overall outreach efforts.

Decisions in the Field

Too often, public involvement is structured so that community relations staff simply record public concerns, take them back to whoever can make the decisions, and return, some indeterminate time later, with a response. Expanding the limits of the authority for field managers to deal with citizens' concerns provides a great deal of credibility.

Inter-agency Coordination

Inter-agency coordination takes time and it requires an understanding of agencies' different missions and scopes of authority. It is necessary to include time for interagency coordination in the planning process. Effective inter-agency coordination must be ongoing if disconnections between agencies are not to derail a project.

The Playing Field

Citizens need resources to participate. Public participation, within the current system, takes place on anything but a level playing field. Although Technical Assistance Grants (TAG) are available under the Superfund program, they are only a start for most sites. For large, complex federal facilities, they are wholly inadequate. TAGs time and budget constraints are simply too tight for citizens to play a genuine role throughout this process.

Independent, "Third Party" Experts

Independent experts make any message more believable. They build legitimacy for whatever part of the process they're involved in, if they are truly independent. They have to represent multiple points of view to be effective. This assures the public that the deck isn't stacked.

Communicate Effectively

Information has to be easily obtained, timely, and understandable. This goes beyond Freedom of Information Act and beyond just dumping every non-classified document into a public reading room. There's a tremendous need to put all this information into a meaningful context and to do so on both the national and the site-specific level.

DEMONSTRATION PROJECTS

In 1993 CCEM is initiating a series of demonstration projects designed to develop and test truly integrated approaches to environmental decision-making. These projects include:

Inactive and Abandoned Noncoal Mines

CCEM will collaborate with key stakeholders throughout the West to develop practicable state-specific cleanup programs for inactive mines. Part of the project's efforts aim at compiling the available information on existing state and federal inactive mine waste activities. This information will be used to support more intensive efforts at workshops involving all the major stakeholders concerned about inactive mine waste.

Western Governors' Association Project

The Western Governors' Association Project will help expedite remediation of contaminated Federal facilities in the West and, by example, throughout the nation by facilitating the demonstration, implementation, and commercialization of new, cost-effective environmental restoration and waste management technologies. CCEM will assist in developing and implementing an effective public outreach plan to support this effort.

Internship Program

A series of CCEM internships links undergraduate and graduate students having specific academic and research skills with citizens' groups and environmental managers. This serves as a model of cooperative endeavor and an example of the fruitful exchange possible when a diverse constituency like that of CCEM is involved in dealing with environmental issues. Its focus is on giving future environmental professionals an opportunity to work in a nonprofit setting to help develop solutions to environmental problems.

American Alliance for Environment and Trade Project

CCEM staff are working with DOE's Office of Environmental Restoration and Waste Management to develop a model program, the American Alliance for Environment and Trade Project, to maximize the return on investment in the national laboratories and other technology sources, to develop new cleanup technologies, and to strengthen industrial competitiveness in global environmental technology markets.

APPLICATION TO MIXED WASTE ISSUES

In addition to our activities in inactive mine waste, the cleanup of Federal facilities, the internship program, and the development of innovative environmental technologies, the Center has begun to use the general approach outlined above to assist DOE with seeking solutions to the Department's mixed waste problems.

The Center is working on a multi-phased outreach effort to enable all stakeholders to become more active participants in the discussions surrounding mixed waste characterization, treatment, and/or disposal. The focus of this effort is to facilitate substantive and meaningful dialogue among parties of diverse perspectives and interests, with the goal of aiding DOE to plan a technology development agenda in a way that solves highly complex technical problems, meets the regulatory criteria of state and federal agencies, and is acceptable to the public. It was agreed that stakeholders would be involved in the design, implementation and evaluation of this research agenda and that all activities would take place in an open manner.

The Center has identified a need for DOE outreach as a first step in a comprehensive effort to improve stakeholder involvement. The 1992 Federal Facilities Compliance Act is forging a partnership between federal and state regulatory agencies. That Act stipulates that DOE's decisions about mixed waste are subject to state regulatory requirements. Those regulatory decisions should be made within a framework of open and active public involvement. DOE's technology development research agenda must recognize a role for the states in defining technology needs, selecting specific technologies for demonstration, and overseeing the performance of the technologies being demonstrated. Some means of consensus-building about these problems is essential if DOE is to be successful in meeting its cleanup milestones and schedules. One such consensus-building activity is facilitation by an independent third party such as CCEM. The Center's ability to bring the "key players" to the table is an important resource to help work out solutions for the safe disposal of DOE's mixed waste.

DOE policy makers and representatives of selected states have begun discussions to lay a foundation for improved communication between DOE and the states c ı technology demonstrations and to encourage early, proactive state involvement in technology development activities. CCEM is supporting this effort by expanding the state network and schedule of outreach activities. Eventually, these efforts should lead to partnering among states and DOE to better address the states' collective issues concerning mixed low level waste.

The next phase of the outreach effort will be for a joint states–DOE approach to broaden stakeholder involvement. This might take the form of a series of town meetings on mixed waste technical and policy issues. The Center would follow up these meetings with facilitated workshops. The Center's experience in conducting town meetings would be a significant resource in this activity. We are continuing to build links with the key stakeholders and to create a resource group to review and critique the approaches to public involvement we are developing. These approaches, which incorporate some of the most salient lessons learned from two decades of cleanup as well as lessons learned from CCEM's outreach efforts, will be employed to engage stakeholders in the design of DOE's research agenda for mixed low level waste problems.

The goal of the meetings with the individual states and the follow-up town meetings is to clearly identify any areas of technology deficiencies and areas of strong public concern. These meetings could identify a clear definition of technology and technical needs worthy of more detailed discussions within a workshop format. For example, satisfactory characterization, treatment, and/or disposal of the contents of mixed waste containers involve diverse technical, regulatory, public health and safety issues. Opening containers to characterize the waste presents potential health and safety threats to the immediate workers and to the surrounding population. Technologies and techniques for non-intrusive analysis are not readily available. Further, characterization requirements could vary significantly depending upon the treatment and disposal options selected for a particular site. Decisions on site characterization and treatment/disposal are directly driven by regulatory requirements (including those of the chosen disposal sites), treatment parameters, transportation routes, and, it should go without saying, public acceptability.

If the stakeholders show a high level of interest in more detailed discussion of the issues surrounding mixed waste management, then the Center will facilitate a workshop to allow participants from

environmental organizations, state and Federal regulators, local and state government officials, DOE headquarters and field staff to build consensus about the best approaches for characterization, treatment, and disposal of containerized mixed wastes.

CONCLUSION

Active public participation is a "fact of life" in environmental decision-making. The only real issue is whether the agencies responsible for environmental management will be proactive in their efforts to assist in this process or whether they will do so only reluctantly, in response to the strict demands of legislation or threat of litigation. When public participation and regulatory factors are considered in the earliest stages of the decision-making process, especially prior to and during technology selection, public understanding confidence increase. This in turn should foster more efficient, cost effective approaches to DOE's mixed waste problems.

Nothing this article recommends is a simple panacea. None of the "principles of public involvement" or the activities undertaken to help build a consensus for action on mixed waste represent a cure-all. We acknowledge that there may be intractable problems associated with mixed waste. However, until we systematically implement and evaluate approaches like those that TRIP will be doing in the coming years, environmental management seems doomed to repeat past mistakes in a variety of guises and circumstances. TRIP's great virtue is that it consistently integrates the key stakeholders and the relevant regulatory context into the decision-making process. Until we begin doing this in a systematic fashion any efforts to streamline the process and to develop and deploy solutions to mixed waste face an uncertain future at best. Given that resolving the problems associated with mixed waste is essential to the cleanup of the DOE Complex we could do far worst than to begin by trying to build consensus among those whose buy-in is essential before we can move forward.

MANAGEMENT OF MIXED WASTES IN CANADA

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ABSTRACT. Mixed radioactive and hazardous waste is generated at the rate of approximately 750 m^3/y which is about 9% of the annual low-level radioactive waste generation rate. As mixed waste is not a formal classification in Canada, it is managed as low-level radioactive waste. Regulation of mixed waste is thus under the jurisdiction of federal Atomic Energy Control Board, and is performed through a joint consultative process with relevant federal and provincial ministries of the environment. The joint consultative approach has worked satisfactorily thus far in the management of mixed waste in Canada.

INTRODUCTION

In Canada, there is an integrated nuclear industry ranging from uranium mining, refining, fuel fabrication, nuclear power generation to production and use of radioisotopes for medical, academic and industrial purposes. The initial generation of low-level radioactive waste was associated with the refining of radium at Port Hope, Ontario, in the 1930's. As the Canadian nuclear program developed after the second world war, production of uranium became the most important component of the Port Hope plant. At about the same time, research and development began at the Chalk River Laboratories (CRL) of Atomic Energy of Canada Limited (AECL), on the applications of nuclear energy for electricity production and the use of radioisotopes. At present, there are twenty-two CANDU (CANada Deuterium Uranium) nuclear power plants in operation generating about 16,000 MW of electricity, with supporting nuclear fuel cycle facilities, 10 research reactors, and about 4,000 radioisotopes licenses. All of these sectors generate radioactive wastes. Some of these wastes also contain varying amounts of chemically or biologically hazardous components.

It should be noted that these mixed radioactive/hazardous wastes do not have a formal designation or classification in Canada. They are managed as low-level radioactive wastes. In Canada, low-level radioactive wastes are defined as all radioactive wastes other than used nuclear fuel wastes and uranium mill tailings.

In 1982, the government of Canada established the Low-Level Radioactive Waste Management Office (LLRWMO), as an independent agent of the federal government to carry out the relevant federal responsibilities for low-level radioactive waste management. The LLRWMO is operated by Atomic Energy of Canada Limited (AECL) through an agreement with the federal department of Energy, Mines and Resources (EMR). EMR is responsible for national policy for energy, including nuclear energy and consequently, radioactive waste. As a part of its activities to support EMR's initiatives in developing a national strategy for low-level radioactive waste disposal, the LLRWMO has recently carried out several

assessments on the inventory, generation rate and management practices for the low-level radioactive waste in Canada.

MIXED WASTE GENERATION

The annual accumulation of all low-level radioactive waste in Canada is approximately 8,500 m^3 (1). This volume represents waste which is presently being stored after it has been treated and conditioned. Waste volume as-generated is about 50% higher. It should be noted that many generators have adopted a policy for improving waste management practices and reducing generation of waste at source. For example, Ontario Hydro, which currently operates 20 CANDU reactors, and is a major generator of low-level radioactive waste, plans to reduce waste volume by 25% by 1995, and 50% by 2000.

According to a recent survey carried out for the LLRWMO, mixed waste generators produce approximately 750 m^3 of mixed waste annually (2). This represents about 9% of the total annual production of low-level radioactive waste. The universities and hospitals are the largest generators of such waste and account for about half of the total mixed waste volume (Fig 1). Other major mixed waste generators are: nuclear utilities (20%), uranium refining and conversion plants (12%), and radioinuclides users in industry (12%). Nuclear fuel manufacturing and R&D by AECL together contributes a small amount (5%). Typically, mixed wastes include incinerator ash, hydraulic and lubricating oil, organic solvents, scintillation fluids, metals, animal carcasses, asbestos, etc.

The nature and characteristics of hazards from mixed waste depend on the source of generation of the waste. For example, the radiological hazard from mixed wastes from universities and hospitals is due to ^{3}H, ^{14}C, ^{32}P, ^{125}I and Tc-99m etc., some of which have very long half-lives. The non-radiological hazard is from

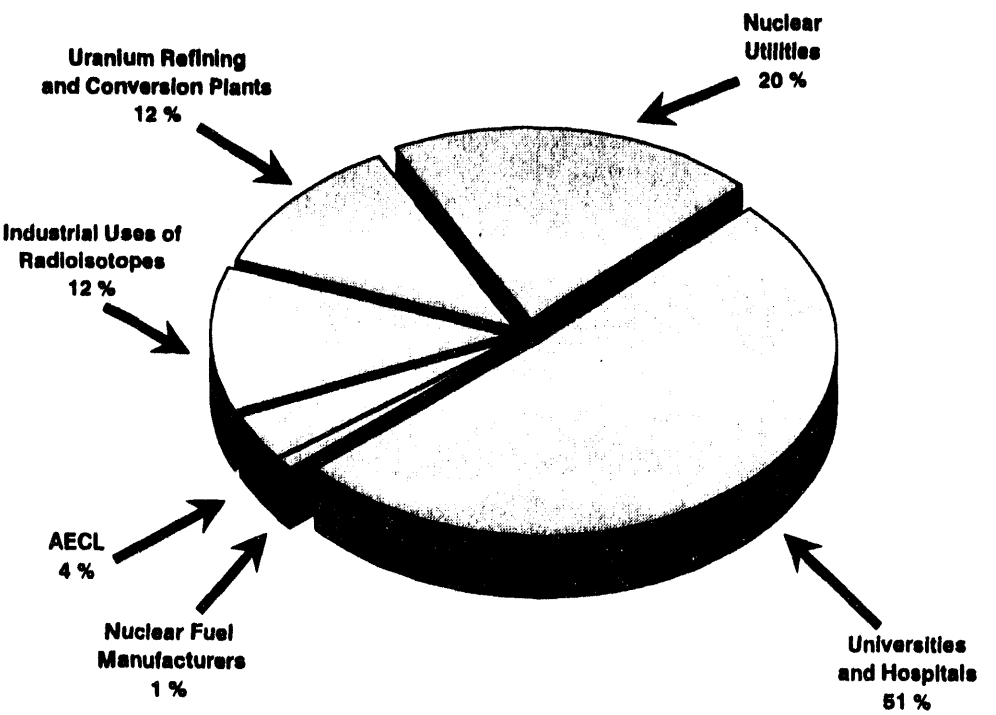

Figure 1. Mixed Waste Generation

organic liquids, and biological materials. Mixed wastes from nuclear power production contain radionuclides, such as ^{3}H, ^{14}C and other fission and activation products. The non-radiological hazard is due to organic liquids, lead, asbestos and oil. Mixed wastes from uranium refining, conversion and fuel fabrication are primarily contaminated with natural uranium. Organics and oil comprise the non-radiological hazard.

In order to enhance the quality of existing data and information on low-level radioactive waste, including mixed waste, the LLRWMO has initiated a comprehensive survey of waste generators. A report compiling the detailed information collected from this survey is expected to be available by the end of 1993.

REGULATORY APPROACH

Under the Atomic Energy Control Act proclaimed in 1946, the federal government has responsibility for the control and supervision of the development, application and use of atomic energy. This Act led to the formation of the federal regulatory agency, the Atomic Energy Control Board (AECB), with responsibility for regulating health, safety, security and environmental aspects arising from nuclear activities. The AECB administers the Atomic Energy Control Act and the regulations under the Act. Radioactive wastes, including mixed wastes, are thus under the regulatory control of the AECB.

On the other hand, hazardous wastes are primarily under the regulatory control of the federal Department of the Environment (Environment Canada) and provincial ministries of the environment.

The AECB routinely regulates all low-level radioactive wastes including mixed waste. It recognizes that the non-radiological hazards in mixed waste, can have effects on the activities which are regulated by other jurisdictions. As a result, the AECB has adopted a policy of joint or cooperative process for the regulation of nuclear activities including mixed waste management. In this process, the AECB distributes to all other relevant regulatory agencies the pertinent information so that input into the AECB licensing decisions is comprehensive. This extends to inspection where, in many instances, inspectors from other regulatory agencies accompany AECB inspectors in the discharge of their duties. As a result, the license issued by the AECB not only incorporates the requirements with respect to radioactive material, but also any additional requirements identified by other regulatory agencies.

In addition to this consultative approach, there is a formal Memorandum of Understanding (MOU) between the AECB and Environment Canada. Under the terms of this agreement, the AECB and Environment Canada agree to cooperate in the development and adoption of standards and objectives for the protection of the natural environment which relate to the use and application of nuclear energy. In general, the goal of Environment Canada is to develop standards and objectives for the permissible concentrations of radioactive and other toxic substances related to nuclear energy as well as to monitor for radioactive and other toxic substances, in cooperation with other agencies, outside the boundaries of nuclear facilities. The purpose of the AECB is to seek the advice of Environment Canada in environmental matters and take into account their standards and objectives in exercising its regulatory functions. The two parties also agree to consult in other situations where both have regulatory interest.

Similar Memoranda of Understanding (MOU) exist between the AECB and several provincial regulatory agencies for cooperation and consultation in regulating nuclear activities.

The joint regulatory process for mixed waste is depicted in Fig. 2. The primary regulatory responsibility and control is held by the AECB with appropriate feedback from other relevant agencies. At the present time, neither Environment Canada nor the provincial regulatory agencies regulate the storage, use or disposal of radioactive materials and wastes. The joint regulatory process for mixed waste in Canada has worked satisfactorily thus far.

The transportation of radioactive materials is another example where the mutual consultation and sharing of responsibilities has successfully worked in dealing with radioactive materials. Under the Atomic Energy Control Act, the AECB has made regulations governing the transportation of radioactive materials. These regulations, which are based on the recommendations of the International Atomic Energy Agency, deal with radiological protection for health, safety and protection of the environment during transport. The AECB's Transport Packaging of Radioactive Materials (TPRM) Regulations also reference the Transport of Dangerous Goods (TDG) Regulations of Transport Canada. These TDG Regulations apply to all hazardous materials which are divided into nine classes of which Class 7 is radioactive materials. In the TDG Act and Regulations, radioactive materials are defined in terms of the AEC Act and the TPRM Regulations. The TDG Regulations also reference the TPRM Regulations for application to transportation.

Thus the regulatory control for the transport of radioactive materials (including wastes) is shared between the AECB and Transport Canada. In essence, Transport Canada is responsible for the operational activities of the means of transport such as documentation, initial emergency response and stowage in the means of transport. The AECB is responsible for the radiological aspects such as worker exposure to radiation, packaging, labelling and marking of the radioactive material and receipt of consignments. By reference to each others' regulations, Transport Canada and the AECB ensure that there is no conflict in requirements and that both primary and any subsidiary hazards are taken into account. It should be noted, however, that the radiation hazard takes precedence during transport. A memorandum of agreement is in place between Transport Canada and the AECB to facilitate the smooth implementation of their respective responsibilities for the transportation of radioactive material.

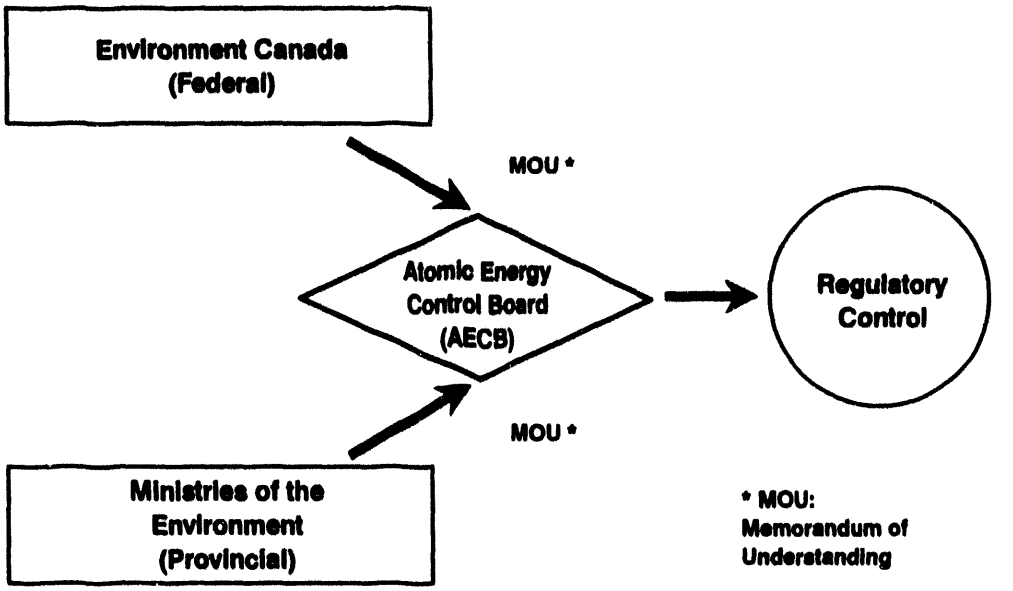

Figure 2. Joint Regulatory Process for Mixed Waste

CURRENT MANAGEMENT PRACTICES

All low-level radioactive wastes including mixed waste are currently in storage, although initiatives are underway to establish disposal facilities for the stored wastes. Chalk River Laboratories (CRL) of Atomic Energy of Canada Limited (AECL) is the only organization which provides commercial storage services primarily for small volume generators across the country.

The majority of the mixed wastes from uranium refining and conversion facilities are either recycled to uranium mills or stored at the site pending development of disposal options. A relatively small quantity is sent for storage at CRL. All mixed wastes from nuclear fuel fabrication activities are sent for storage at CRL.

Mixed wastes from all Ontario Hydro nuclear plants are processed and stored at its centralized facility at the Bruce Nuclear Power Development near Lake Huron. Mixed wastes from the other two utilities (Hydro-Quebec, Quebec and New Brunswick Power, New Brunswick) are managed at the respective plant sites. The majority of liquid mixed wastes (eg. lubricating oils, organic solvents) are stored at the sites awaiting development of more effective treatment technologies.

Mixed wastes from the R&D activities of AECL are processed and stored at the sites. AECL also has a program at its facilities at Chalk River Laboratories to improve treatment technologies for liquid mixed waste.

Most of the mixed wastes from the production and use of radioisotopes such as those produced in hospitals, universities, pharmaceuticals, and industrial users, are normally held for a period of time to allow radioactive decay and then disposed of without further restrictions. Wastes containing significant concentrations of long-lived radionuclides are collected, often through brokers, and shipped to AECL's Chalk River Laboratories for storage.

FUTURE MIXED WASTE DISPOSAL

As mentioned above, mixed waste is currently stored in AECB licensed facilities operated by major waste generators. Some major generators have initiated programs to locate and construct disposal facilities for low-level radioactive wastes. These facilities will contain mixed wastes, and it is important that the hazardous components be taken into consideration in the design of these facilities. Because the risk associated with the radioactive component diminishes with time, it is possible that over the long-term, the non-radioactive components will pose the greatest risk. It is thus essential that the chemical and biological hazard of mixed waste be identified and adequately considered in the performance assessments for disposal facilities.

Disposal of mixed waste can be done either as radioactive waste or as hazardous waste as shown schematically in Fig. 3. If the waste contains a significant quantity of radioactivity and poses more than de minimis risk as defined by the AECB (3), waste would be disposed of at an AECB regulated facility. On the other hand, if the radioactivity level decays or can be reduced, to insignificant levels, so that disposal of the waste would represent only a de minimis risk, then the waste is exempted from further regulatory control by the AECB (3). Once exempted, the waste is considered as only hazardous and can be directed to provincially regulated facilities for disposal. Currently, the AECB uses a criterion of de minimis radiation dose to individuals of 0.05 mSv/y for deciding such exemptions on a case-by-case basis, provided that the radiological impact is localized and the potential for exposure of large populations is small.

If the waste is classified as non-hazardous, it can be disposed of at landfills. If it contains hazardous components which cannot be removed or treated to make it non-hazardous , the waste will be disposed of

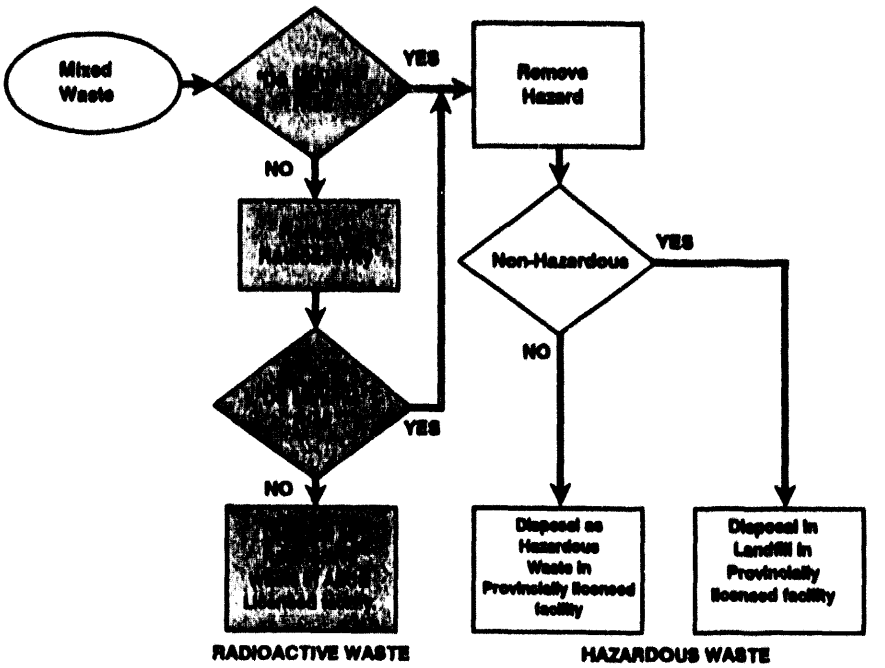

Figure 3. Mixed Waste Disposal.

as hazardous waste. Disposal of hazardous waste is a well established practice. In principle, it is thus desirable to treat or process mixed waste to the greatest extent possible to segregate the radioactive component from the hazardous waste component, so that the hazardous waste can be disposed of through established facilities.

There is, however, an area of concern for regulatory inconsistencies. Where mixed waste is exempted by the AECB from further regulatory control as de minimis waste, it passes in principle, from federal to provincial jurisdiction for hazardous waste regulation. So far, generators do not seem to have taken much advantage of the de minimis disposal options. One of the reasons cited is that some provincial authorities consider the AECB exempted de minimis waste as still radioactive waste according to their own criteria, and thus they do not wish to regulate the waste.

Thus difficulties can arise when regulatory requirements are developed independently by different agencies. It is only natural to expect that the requirements will have areas where they differ if they are developed separately and with different objectives. There is a need to identify such interface areas and develop consistent approaches. For example, it is important that the regulatory agencies reach consensus on the level at which the radioactivity of wastes no longer pose a threat to health or the environment. That is, a consistent definition and application of the de minimis principle is required. The development of rational technologically driven criteria and risk assessment methods that would be applicable to both radioactive and non radioactive wastes on a common basis would assist this process.

CONCLUSIONS

Thus far, the management of mixed waste in Canada has proceeded satisfactorily. The primary regulatory agency is the federal Atomic Energy Control Board (AECB), which exercises its regulatory function by drawing information through a consultative process with relevant federal and provincial authorities. This consultative process has proved to be successful in regulating mixed wastes in Canada.

Mixed wastes are presently in storage. Initiatives are, however, underway to make a transition from storage to disposal. For this transition, it is important that all areas of concern for potential regulatory inconsistencies be identified and resolved. In particular, a consensus is desirable among the relevant federal and provincial regulatory agencies on the development and application of de minimis principle and risk assessment methodology for mixed waste.

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IMPACTS OF BRC DISPOSAL OF ACTIVATED OIL FROM THE STANFORD LINEAR ACCELERATOR CENTER

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ABSTRACT. The purpose of this paper is to demonstrate that the disposal of 2 m^3 of non-RCRA vacuum pump oil, containing trace quantities of tritium, as hazardous waste will not impact workers, the general population or the environment. The oil contains approximately 15,000 pCi/L of tritium, well below the Clean Water Act standard of 20,000 pCi/L in drinking water. The impact of incineration and disposal of this waste was determined using IMPACTS-BRC, Version 2.0.

The dose estimates from the IMPACTS-BRC code were used to determine potential risk to the surrounding population. Normally, in a population of 100,000 people, 17,000-21,000 will die of cancer over a 70 year period. The highest dose increase from the disposal of this waste, using "worst case" conditions, may cause this value to increase to 17,000.00053-21,000.00053.

INTRODUCTION

This report presents the results of analyses of the potential radiological impacts from the incineration and/or disposal of activated vacuum pump oil. Although the oil is not regulated under the Resource Conservation and Recovery Act (RCRA) it is regulated as a California List hazardous waste. The oil was collected during routine vacuum pump maintenance and replacement at the Stanford Linear Accelerator Center (SLAC) located in Menlo Park, CA. This report discusses the whole body effective dose equivalent (hereafter referred to as "dose" and measured in mrem/yr or person-mrem/yr) associated with the disposal of this waste. Persons who might be exposed during this operation include the workers and handlers engaged in the loading, transportation, and disposal and members of the general public. Offsite airborne and ground water effects are examined along with impacts to intruders of the disposal site who could become exposed after the administrative loss of control at the disposal site (site closure).

The analyses described in this report is based on the IMPACTS-BRC (1) computer program which was developed for the U.S. Nuclear Regulatory Commission to evaluate petitions to classify specific waste streams as below regulatory concern (BRC). Exposure mechanisms evaluated by IMPACTS-BRC include direct exposure to beta radiation, ingestion and inhalation of radionuclides, and environmental modeling parameters.

The radiological characteristics of the activated vacuum pump oil are described under Waste Characteristics. The IMPACTS-BRC computer program used to estimate the doses from this disposal at a hazardous waste incinerator and/or landfill is described in the section entitled Methodology and Analysis. The results and discussion from the dose analyses are then presented, followed by the conclusions.

WASTE CHARACTERIZATION

The SLAC is located on 426 acres of Stanford University land in an unincorporated area in the extreme southern part of San Mateo County, California. SLAC operates a 2-mile long Linear Accelerator (LINAC) capable of accelerating electrons and positrons into the GeV energies.

During the operation of the LINAC, high-energy gamma-rays are produced. These gamma rays interact through (gamma,n) reactions producing high-energy neutrons which are thermalized and absorbed by hydrogen in the vacuum pump oil. This process creates tritium , ^3H. The Positron-Electron Project (PEP) ring was dismantled to allow for the construction of the PEP II. The vacuum pumps used in the accelerator were drained, and in some cases replaced. The oil from these pumps accumulated to approximately 71 ft^3 (~2 m^3) and is stored in 55 gallon drums.

Liquid Scintillation Analysis (LSA) on the oil was performed at Controls for Environmental Pollution (CEP), located in Santa Fe, NM in July 1991. The results of CEP's analysis are shown in Table 1. The minimum detectable level for the analysis was 500 pCi/L. Process knowledge of the beam characteristics and location of the vacuum pump oil with respect to the beam, indicate that these samples were taken from areas which have the maximum levels of tritium. Note that all the samples are below the maximum permissible tritium level of 20,000 pCi/L in federal drinking water standards (2).

Table 1. Liquid scintillation analysis.

Sample Identification No.	Results (pCi/L)
01-PS Oil	13056
02-PS Oil	15888
03-PS Oil	15207
Average	14717

METHODOLOGY AND ANALYSIS

Estimated doses to individuals and the population from the incineration and/or disposal of this radioactive waste oil in a hazardous waste incinerator/landfill were calculated using the IMPACTS-BRC computer program. The features of the IMPACTS-BRC computer program for dose calculations are described in this section.

IMPACTS-BRC (2) Version 2.0 is a modification of the Version 1.0 computer program designed to estimate radiological impacts from very low-level radioactive waste disposed by using less restrictive disposal options. The code was developed to evaluate petitions to exempt very low-level radioactive waste streams from NRC (and Agreement States) regulation.

IMPACTS-BRC waste processing options include onsite and offsite incineration, sanitary landfill disposal, and hazardous waste landfill disposal. Radiological impacts to workers, environment, and the offsite general public are calculated for the transportation, incineration, and disposal of the waste. Doses to individuals who intrude on a disposal site after site closure and engage in agricultural or construction activities are calculated, as well as long term impacts to intruders and offsite individuals from ground water pathways. The outputs from IMPACTS BRC include several abbreviations to identify the dose results; these are listed in Table 2.

Table 2. Definitions of dose result abbreviations.

Impact Scenario	Units*	Definition
Transportation:		
TR-MAX	a	Impacts to maximum transport worker
TR-OCC	b	Total impacts to transport workers
TR-POP	b	Impacts to population along transport route
Intruder:		
INT-CO	a	Intruder-construction impacts
INT-AG	a	Intruder-agriculture impacts
Exposed Waste:		
IN-AIR	b	Intruder-initiated airborne impacts
ER-AIR	b	Erosion-initiated airborne impacts
INT-WAT	a	Intruder-initiated waterborne impacts
ER-WAT	a	Erosion-initiated waterborne impacts
Incineration and Operation:		
IC-POP	b	Population impacts from incineration
IC-IND	a	Off-site individual impacts from incineration
IC-WOR	b	Total worker impacts at incinerator
IC-MWR	a	Maximum worker impacts at incinerator
OP-IND	a	Off-site individual impacts from disposal operations
OP-WOR	b	Total worker impacts at disposal facility
OP-MWR	a	Maximum worker impacts at disposal facility
LA-OPS	a	Operational leachate discharge impacts to individual
LA-PVF	a	Leachate overflow impacts to individual
LA-AIR	b	Population airborne impacts due to evaporator impacts

* a=mrem/yr; b=person-mrem/yr; c=person-mrem/30 yrs
Source: NUREG/CR-3585, Vol. 2, Table 20 (3).

Three data input files (TAPE1.DAT, TAPE2.DAT, and TAPE5.DAT) are used in executing the IMPACTS-BRC computer code. The input files exist as ASCII data in fixed-field format. TAPE1.DAT contains nuclide-specific data, such as retardation coefficients, current dose conversion factors (DCFs) for

calculating radiological impacts from ingestion, inhalation, external volume source, external area source, and external air immersion source. The DCFs were obtained from ICRP-30, Parts I-IV, and the DCFs for the volume source were calculated using the computer program MICROSHIELD. In general, this file would not require user editing, and was not changed for the dose calculation for this report.

The second input file, TAPE2.DAT, contains data for the reference environments and facilities used by the code. The data in this file may require user editing for specific situations and operating parameters chosen at a given facility. In TAPE5.DAT, discussed below, a parameter called Data Index (IDAT) was chosen to be "2". This caused the site parameters in TAPE2.DAT to default to a "worst case" scenario, i.e., a very poor performance site. This increased the level of conservatism.

The population density default value used by IMPACTS-BRC to calculate the population dose from transportation is 610 persons/mi^2. Although the surrounding Stanford area is densely populated, much of the route from the SLAC to a hazardous waste landfill would be through areas with lower than average population density. Therefore, the default value of 610 persons/mi^2 represents a conservative estimate along the route.

The input parameters also included the distance to the disposal site. A variety of hazardous waste disposal sites could be used, however, the distance only effects the dose to the transportation worker (driver) and the surrounding population. Since the only radionuclide is tritium, a beta particle emitter, there is no impact because the beta particles cannot penetrate the steel drum. Therefore, the distance is of no consequence, however, a value of 600 miles was used to approximate a trip to a disposal facility, e.g., in Utah. In addition, only one truck will be used to haul the 2 m^3 of oil to the disposal site. It was also assumed that the average speed of the disposal vehicle will be 45 mph.

IMPACTS-BRC dose calculations are based on the effective radionuclide concentration in the waste, which is the quotient of the radioactivity in curies disposed annually divided by the volume of the non-radioactive constituents. IMPACTS-BRC uses a default value of 9.1 x 10^4 m^3/yr for the volume of waste disposed annually. The default landfill occupies 150 acres, operates 260 days a year for 20 years. Applicable regulations require 30 years of institutional control after site closure (4). None of the calculations in this report took credit for this 30 year period, i.e., after the 20 year closure, there was no added institutional control. The modeling assumes that approximately 58 people work at the facility.

The reference hazardous waste incinerator is assumed to be a rotary kiln design, which has a maximum capacity of 2.5x10^4 m^3/yr. During incineration, 90 % of the tritium is assumed to be lost out the stack. The incinerator requires 18 people to operate. A complete description of the reference facilities can be found in the IMPACTS-BRC Version 2.0, Program User's Manual.

The code assumes a default of a continuous disposal operation rather than a one time disposal. Since the intent of this model was a one-time disposal operation, parameters were chosen which reflect an Operational Life of the Facility for one year (ILFE=1). After which time it would be closed (i.e., no additional radioactive waste oil would be introduced), and institutional control would be given for nineteen years (IINS=19). These parameters more closely approximate the condition of sending a one time waste stream (non-reoccurring), which would then be administratively controlled for the remainder of the landfill lifetime (assumed to be 20 years). As noted above, no credit is taken for the required 30 year post-closure control. The code assumes no leaching occurs during the operation of the landfill, but does allow for leaching during the Institutional Control period. Therefore, the parameter choice has allowed for leaching to occur earlier than would be expected, therefore adding more conservatism to the analysis.

The third input file is TAPE5.DAT which defines the waste type and treatment/ disposal options. This file must be created by the user by choosing options available or inputting values appropriate to the specific waste type. As noted above, the Data Index coefficient in TAPE5.DAT was used to default the facility

parameters to a "worst case" scenario. The file also describes the physical, chemical, and radiological

Table 3. Input parameters.

Data Input	Printout Name	Parameter Name	Value	Comments
[TDIS(IQ)]		Transportation Distance to Facility	600	Miles
[TVEL(IQ)]		Transportation Velocity to Facility	45	Miles/hour
[ILFE]	LIFE	Operational Lifetime of Facility	19	Years
[IR]	REGN	Regional Index	02	Southeast: humid, moderate soil permeability, moderate population density
[IPOP]	IPOP	Facility Environmental Index	02	Urban Site
[IOFL]	OVFL	Overflow Index	01	Calculate overflow impacts
[IDAT]	DATA	Disposal/Treatment Population	02	Environmental parameters for poorest performing disposal site; most conservative approach
[IINS]	INST	Institutional Control Period	19	Years
[NSTRD]	NSTR	Number of Wastestreams	01	Vacuum Pump Oil
[BAS(1,1)]		Mass of Wastestream	1.8	Mg Oil
[BAS(1,2)]	Density	Density of Wastestream	0.9	Mg/m^3
[BAS(1,3)]		Volume of Wastestream	2.0	meters
[ID]		Dispersability Index	03	Severe
[IA]		Accessibility Index	01	Ordinary Waste-01
[IK1]		Packaging Index	01	Metal Containers
[IK2]		Packaging Recycling Index	0	Not Recycled
[IP]	Process	Processing Index	01/02	Disposal-no sorting-01/Incineration and disposal-02
[IX1]		Number of shipping vehicles	01	Maximum route exposure to handler
[IX2]		Percent of Load Radioactive	100	
[IX3]		Number of Incinerators	1	
[IX4]		Number of Disposal Facilities	1	
[IC1]*		Percent of Load Combustible	100	Oil
[IC2]*		Percent of Load Glass	0	
[IC3]*		Percent of Metal Waste	0	
[IC4]*		Percent of Load that is other Waste	0	

*Note: Indices [IC1]-[IC4] are only used for sorting and recycling. Valid if IP>2 .

TAPE5.DAT parameters were chosen to ensure conservatism in the results of the dose calculations. The Region Index was selected so that doses were calculated for a landfill at a humid location with permeable soil, to increase the estimated doses for ground water pathways. The landfill was assumed to be located in an urban environment, resulting in larger population doses than if the rural environment had been chosen.

characteristics of the waste stream(s). The TAPE5.DAT parameter values used for these dose calculations are shown in Table 3.

RESULTS AND DISCUSSION

Potential radiation doses to maximum exposed individuals and the general public from disposal of activated SLAC vacuum pump oil as hazardous waste were evaluated using the IMPACTS-BRC computer program. Input parameters for the computer calculations are shown in Table 3. Two separate scenarios were evaluated using basic input parameters discussed above. Table 4 is the tabulation of doses received based on incineration of the oil; Table 5 is the tabulation of doses received based on simply disposing of the oil in the drums.

Table 4. Individual and population doses from incineration.

Impact Scenario*	Units	Results
Transportation Impacts:		
TR-MAX	mrem	0.00
TR-OCC	person-mrem	0.00
TR-POP	person-mrem	0.00
Operational Impacts:		
IC-POP	mrem	2.2×10^{-3}
IC-IND	mrem	6.5×10^{-8}
Ground Water Impacts:		
Intruder Well(20 y)**	mrem/yr	8.1×10^{-6}
Population-Well(40 y)**	mrem/yr	1.5×10^{-8}
Population-Surface Water(60 y)**	mrem/yr	3.4×10^{-11}

* For definitions of abbrivations, see Table 2

** years after loss of institutional control

The largest individual dose from incineration of the oil will be to an intruder who uses a well on the site in 20 yrs. This intruder could receive a maximum annual dose of 8.1 nrem. Individual offsite impacts from the incinerator operation would cause a dose of 6.5×10^{-8} mrem. The model allowed the incinerator to be located in an Urban area (to add conservatism), which causes the total population effect from the incinerator to be 2.2×10^{-3} person-mrem. Note that the operational impacts are assumed to be on an annual basis, however the analysis was performed for a one-time incineration/disposal. Therefore, the units on the operational impacts doses are actually in mrems and person-mrems, not per year doses. As noted earlier, the transportation doses are zero since the beta particles cannot penetrate the steel drums. All other pathways cause doses which are less than those discussed.

The largest individual dose from straight disposal of the oil will also be to an intruder who uses a well on the site in 20 yrs. This intruder could receive a maximum annual dose of 8.1×10^{-5} mrem. The maximum individual worker dose is 2.0×10^{-7} mrem, resulting in a total worker dose of 1.2×10^{-5} mrem. All other pathways cause doses which are less those discussed.

There are two scenarios which will maximize the exposure to any individual from disposal/incineration operation. The first scenario involves the person who lives just outside the boundary of the facility and remains their throughout their life (i.e., 70 years). The second scenario involves the person who lives just offsite during the initial operation of the facility and then moves onto the site after site closure (Intruder scenario). In Figs 1 through 4, the dose to these individuals are presented for both the incineration and disposal options. The bar labeled as "Operations" is a one time dose caused by the operation of the incinerator/disposal facility. The units on this bar is actually mrem, not mrem/yr. The bars in Figs 1 and 2, at 20, 40, etc. years, represent the sum of the well and surface water impacts offsite. In Figs 2 and 4, these bars represent an intruder well.

The cumulative dose to the individuals in these scenarios can be approximated by summing the operation impacts, along with the doses which are indicated at 20 year increments. By assuming a linear relationship between data points, a cumulative dose can be determined by averaging between two points and multiplying by 20 years (the span between points). For example, in Fig 4, the 40 year sum of the surface and well water doses is: 1.46×10^{-08}; at 60 years this value is 1.32×10^{-09}. The cumulative dose for an individual during this time period can be calculated by the following methodology:

Table 5. Individual and population doses from disposal.

Impact Scenario*	Units	Results
Transportation Impacts:		
TR-MAX	mrem	0.00
TR-OCC	person-mrem	0.00
TR-POP	person-mrem	0.00
Operational Impacts:		
OP-IND	mrem	3.5×10^{-17}
OP-WOR	mrem	1.2×10^{-5}
OP-MWR	mrem	2.5×10^{-7}
Ground Water Impacts:		
Intruder Well(20 y)**	mrem/yr	8.1×10^{-5}
Population-Well(40 y)**	mrem/yr	1.5×10^{-7}
Population-Surface Water(60 y)**	mrem/yr	3.4×10^{-10}

* For definitions of abbreviations, see Table 2.
** years after loss of institutional control.
(Maximum dose levels from loss of institutional control to 20k years.)

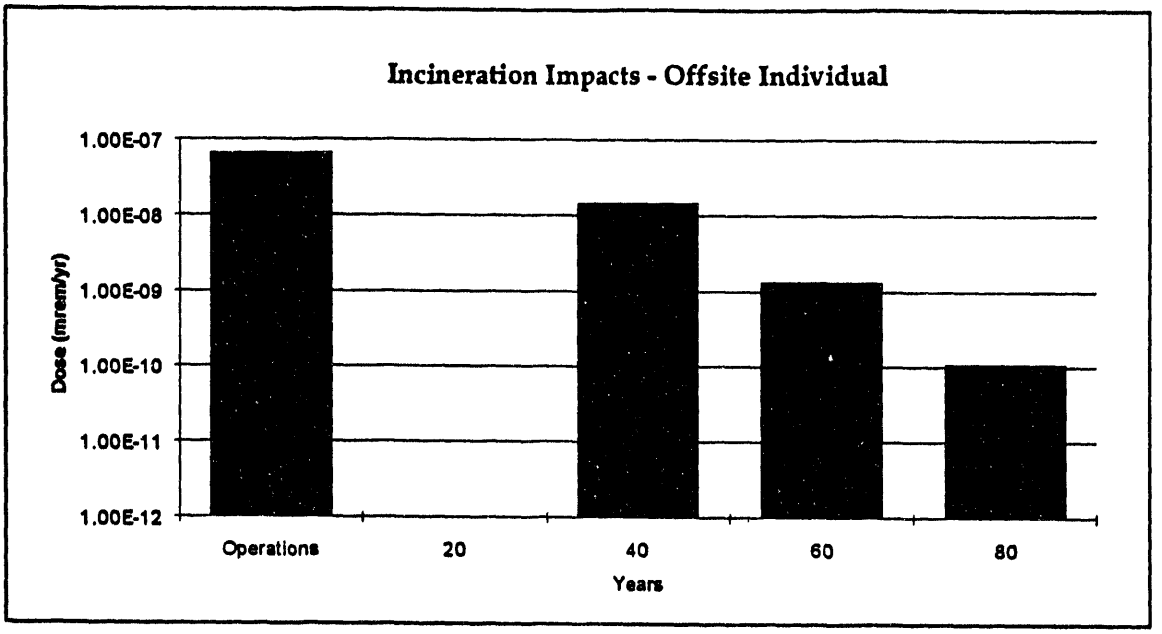

Figure 1. Incinerator impacts - offsite individual.

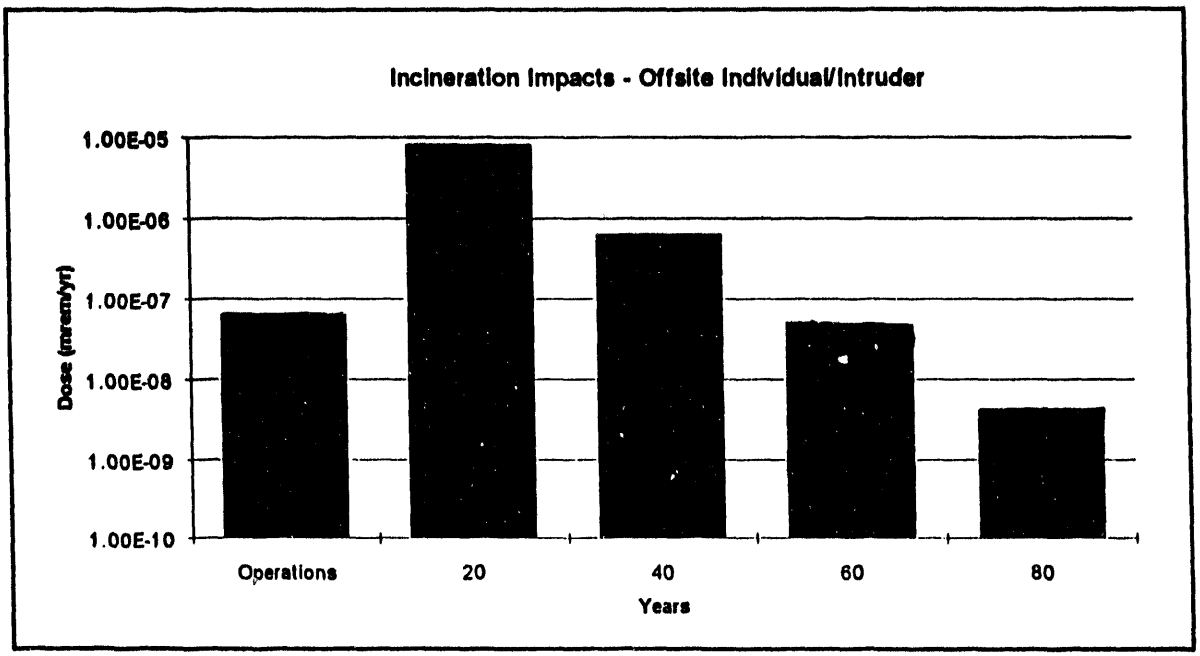

Figure 2. Incinerator impacts - offsite individual/intruder.

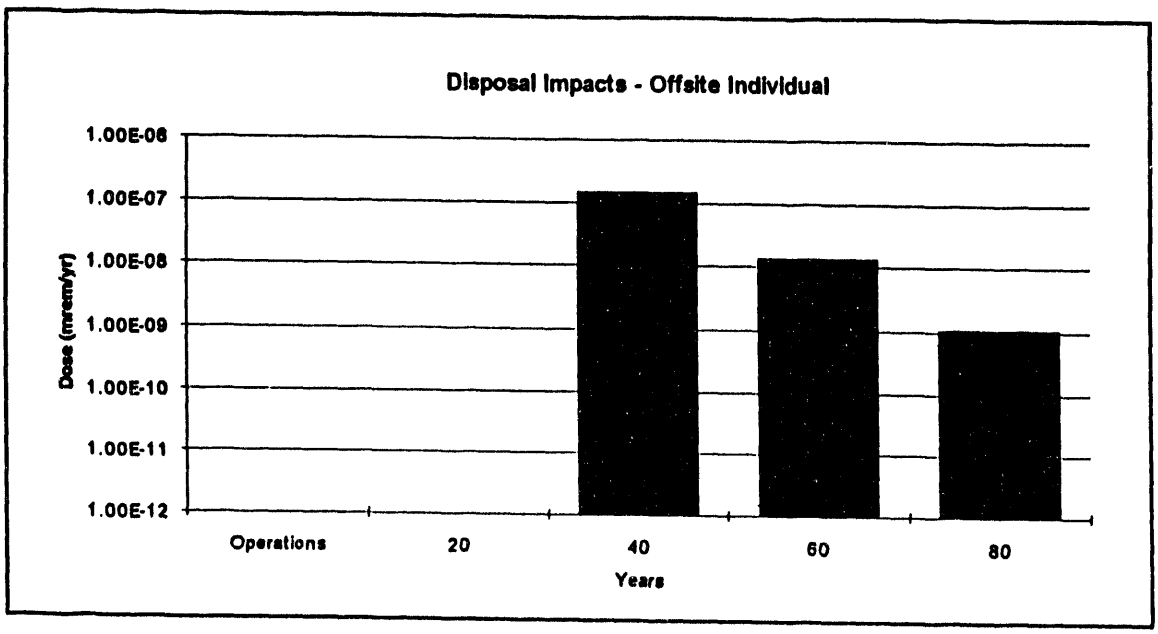

Figure 3. Disposal impacts - offsite individual.

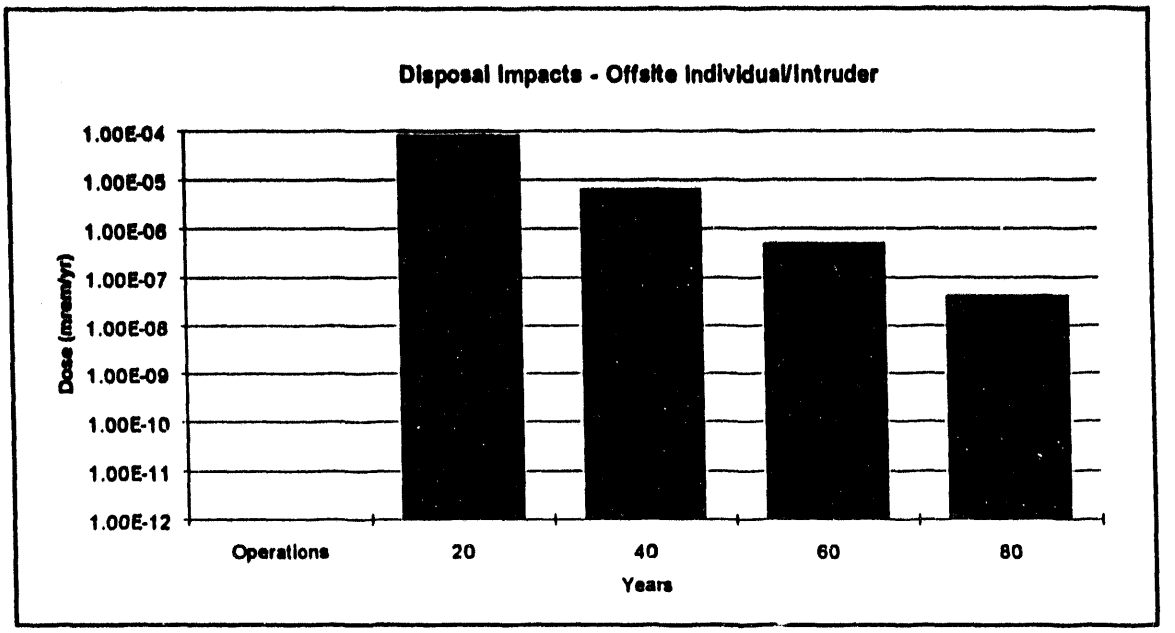

Figure 4. Disposal impacts - offsite individual/intruder.

$$Dc = [(PW40+PS40)+(PW60+PS60)]x10 \quad (1)$$

Where:

Dc = Cumulative Dose, during the time from t=40 to t=60
PW40 = Dose due to Offsite Well Water (mrem/yr) @ t=40 years
PS40 = Dose due to Offsite Surface Water (mrem/yr) @ t=40 years
PW60 = Dose due to Offsite Well Water (mrem/yr) @ t=60 years
PS60 = Dose due to Offsite Surface Water (mrem/yr) @ t=60 years

By summing the incremental doses from the offsite water pathways to the initial operational impacts, the cumulative dose can be approximated. The dose for the intruder scenario can be determined by summing the onsite intruder well pathway to the operational impacts. The results from these calculations can be seen in Table 6. Note that additional impacts to these individuals ranges from 8 to 11 orders of magnitude smaller than the dose they will receive from normal background (5).

Table 6. Dose comparisons of disposal scenarios with normal background.

Scenario[1]	Total Cumulative Dose (70 yrs)	Excess Dose Background
1	$3.8x10^{-7}$	$1.5x10^{-11}$
2	$1.8x10^{-4}$	$7.0x10^{-9}$
3	$3.1x10^{-6}$	$1.2x10^{-10}$
4	$1.8x10^{-3}$	$7.0x10^{-8}$
Background	$2.5x10^{4}$	

The final step in the analysis is to translate the potential impact into a potential for these doses to causes harm to the individuals involved. Cancer deaths caused by excess radiation has been studied since World War II by countries around the world. The Biological Effects of Ionizing Radiation (BEIR) committee has examined these impact studies and compiles data and makes recommendations as to the approach which should be used when modeling radiation effects. The most recent compilation, the BEIR V Report, 1990 (5), notes the inherent difficulty in using the available data for low-level dose calculations. As doses approach background levels, particularly continuous doses, it becomes very difficult to develop meaningful statistics. The rate which can be inferred from the BEIR V report is between $5x10^{-5}$ and $6 x10^{-5}$ excess cancer deaths per 1 mrem/yr of continuous exposure (5). As a matter of conservatism, all calculations will use $6x10^{-5}$. The uncertainties grow larger as these values are applied to doses significantly below the testing value of 100 mrem/yr. All calculations assume a linear extrapolation from 100 mrem/yr to 0.0 mrem/yr (5).

The scenarios examined in this report show an initial population dose from the operation of the incinerator/disposal facility, in addition to a potential continuous ground water dose, either on or off-site. Therefore, it is not straightforward to make a simple excess cancer death rate due to continuous exposure, because the exposure is not constant. After the oil is incinerated/disposed, there is no impact until 20 to 40 years later. As the tritium decays, the potential ground water impact reduces. As a result, a calculation which bases a lifetime continuous dose on the highest (initial) ground water value will largely over-estimate any potential impact. Nevertheless, without extensive weighting factors regarding age and dose, there is no other method is available. The results of using the maximum water pathway value as a continuous dose are shown in Table 7. Note the fractional increase over the normal death rate.

Risk of excess cancer death due to a one-time exposure is approximately $8x10^{-7}$ per mrem. This value is two orders of magnitude lower than the risk for continuous exposure at the same level ($6x10^{-5}$), i.e., death per 1 mrem vs. death per 1 mrem/yr. The individual risk due to the operation of the incinerator is $5.3x10^{-14}$. Assuming that the continuous exposure risk and the one-time exposure risk are cumulative, the total risk to an individual in Scenario 1 is approximately $9.3x10^{-13}$. The total risks in the other scenarios are not affected (within the significant digits of the calculations).

Table 7. Excess cancer death rate.

Scenario[1]	Initial Individual Dose (mrem/yr)	Death Rate (Individual)	Death Rate (Population-100k)	Excess Death Normal[2]
1	1.5x10-8	$8.8x10^{-13}$	$8.8x10^{-8}$	$4.6x10^{-12}$
1a[3]	1.5x10-5	$9.3x10^{-13}$	$9.3x10^{-8}$	$4.9x10^{-12}$
2	8.8x10-6	$5.3x10^{-10}$	$5.3x10^{-5}$	$2.8x10^{-9}$
3	1.5x10-7	$8.8x10^{-12}$	$8.8x10^{-7}$	$4.6x10^{-11}$
4	8.8x10-5	$5.3x10^{-9}$	$5.3x10^{-4}$	$2.8x10^{-8}$
Normal Expectancy	---	$1.7x10^{-1}$-$2.1x10^{-1}$	$1.7x10^{4}$-$2.1x10^{4}$	---

[1] 1 = Incineration: offsite individual
2 = Incineration: offsite individual/intruder
3 = Disposal: offsite individual
4 = Disposal: offsite individual/intruder

[2] Normal = Average of 17,000 and 21,000

[3] Total risk if one-time exposure and continuous are cumulative (see text).

CONCLUSIONS

Since the NRC and the DOE have not developed and enforced a Below Regulatory Concern (BRC) limit, there is no straightforward approach to seek a yes or no answer to problems such as the one this paper examines. There are some guidelines which can be used to help make a judgment concerning the particular

issue of extremely low levels of tritium. A specific exemption is granted for liquid scintillation vials and animal carcasses at 50,000 pCi/gm (6), and the Clean Water Act (CWA) allows 20,000 pCi/L in drinking water. The drinking water level was determined based on the amount a person would drink, and limits their maximum exposure from the tritium to 4 mrem per year. The approach presented in this report clearly indicate a reasonable and responsible method of disposal.

The analysis shows that with the worst case parameters, and gross over-conservatism, the radiological impact of this operation to the workers, public, and environment is negligible by every measurement and scientific principle. By disposing of this oil as an ordinary hazardous waste, as opposed to low-level mixed waste, the DOE will be implementing effective waste minimization policy, and cost-effectiveness commensurate with the degree of hazard associated with the waste.

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MIXED WASTE: A PROPOSED SOLUTION THAT FOCUSES ON THE UNDERLYING PROBLEM RATHER THAN ON ITS SYMPTOMS

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ABSTRACT. Viewed critically, it is apparent that the current mixed waste system is the result of conflicting regulatory regimes. The current mixed waste system is neither functional nor rational. Despite numerous and elaborate attempts by NRC, EPA and DOE to minimize and avoid conflicts between the existing regulatory schemes for radioactive and hazardous waste, the fundamental conflict between Atomic Energy Act and Resource Conservation and Recovery Act requirements remains obvious and unabated. Regulatory paralysis is the result.

In this article, the authors outline some of the key inconsistencies between hazardous and radioactive waste management and disposal requirements and trace the effect these conflicts have had on the existing mixed waste system. The authors argue that mixed waste is of two primary types: waste that is either primarily radioactively hazardous or primarily chemically hazardous and that regulatory requirements should reflect this fact. Hence, where a mixed waste contains only low levels of radioactivity and is primarily chemically hazardous, RCRA controls should predominate. Where a mixed waste contains any significant amount of radioactivity, however, AEA requirements, not RCRA should control.

The primary barrier to such a scheme is the resistance of entrenched regulators and legislators. Under both the Atomic Energy Act, as amended by the Uranium Mill Tailings and Radiation Control Act, and the Nuclear Waste Policy Act, NRC and EPA have cooperated in regulating, respectively, uranium mill tailings and high level waste at sites that will ultimately be owned in perpetuity by DOE. This program has worked for mill tailings for over a decade and there is no reason to believe that a similar program cannot also be successfully applied to mixed waste. Yet until key regulators recognize and accept that the current mixed waste crisis stems not from the unique physical properties of the waste but from their own jurisdictional attitudes, the mixed waste regulatory system can only become more intractable and unworkable.

INTRODUCTION

The current system for control and permanent disposal of mixed waste is neither functional nor rational. Fundamentally ill-conceived, the largely nonexistent mixed waste disposal system is not based on the physical properties of the waste in question but rather on artificial distinctions between the regulatory programs under the Atomic Energy Act (AEA) (1) and the Resource Conservation and Recovery Act (RCRA) (2). Despite the mandate of RCRA section 1006 that RCRA yield to the AEA to prevent any inconsistencies caused by clashing regulatory regimes, neither the Environmental Protection Agency (EPA), the Department of Energy (DOE), nor the Nuclear Regulatory Commission (NRC) has ever realistically addressed the thorough-going inconsistencies between the AEA and RCRA, much less successfully invoked the authority of section 1006. As a result, the management and disposal of mixed waste has become a dilemma.

The basic problem at issue is the failure of Congress and the regulators to acknowledge the essential incompatibility of the AEA and RCRA regulatory regimes. As a result, the regulators have created increasingly complex schemes for avoiding the appearance of incompatibility and millions, if not billions, of dollars are being spent on new technological "fixes" for mixed waste disposal. Yet despite the proliferation of regulations, extensions, clarifications and guidance, the basic situation remains unchanged: permanent disposal capacity for much of the nation's mixed waste is virtually nonexistent, and intractable political and regulatory barriers impede its development.

The solution to the problem is relatively straightforward. It would be based on a recognition of the physical properties of the materials in question, the relative potential hazards associated therewith and the mandate of section 1006 of RCRA. First, given the stringent regulation of low-level radioactive waste under the AEA, for wastes that are significantly radioactive, EPA's assertion of RCRA jurisdiction over the chemically hazardous component of mixed waste provides, at best, a marginal environmental benefit. At worst, it has actually detracted from public health and the environment by unnecessarily diverting resources to deal with a nonexistent problem and by requiring long-term storage of some dangerously radioactive materials. Similarly, for wastes that are primarily hazardous, such as many scintillation fluids containing low levels of radioactivity, assertion of AEA jurisdiction may also be unnecessary and ill-advised.

For a large portion of the mixed waste stream that cannot be readily incinerated and that contains significant levels of radioactivity, the primary long-term hazard is radioactive, not chemical. For these wastes, potentially lethal doses of radioactivity cannot be perceived by human senses and while the toxic components of chemical mixtures can be treated, neutralized or destroyed, radioactivity can only be eliminated by time and transmutation. Some radioactive material can remain actively hazardous for hundreds or even thousands of years.

Where mixed waste is composed primarily of chemically hazardous components, such as fluids that are readily incinerable and contain low levels of radioactivity, NRC and EPA should be directed to exempt such materials from most applicable AEA requirements in a fashion similar to NRC's proposed below regulatory concern policy. Where radioactivity is the primary hazard from mixed waste, the AEA, not RCRA, should assume the dominant role in the regulation of mixed waste. Under such a system, such mixed waste would be subject to only one set of regulations designed to eliminate and minimize, respectively, both the short-term chemical hazards and the long-term radioactive hazards of mixed waste. Disposal could take place at commercial LLRW disposal sites or at DOE owned and operated sites licensed in perpetuity by NRC. EPA would retain both an advisory role through the Federal Radiation Advisory Counsel and an affirmative regulatory role through its authority under Reorganization Plan No. 3 to promulgate "generally applicable standards" for the protection of the public from off-site releases of radioactivity. A role for public participation and oversight at DOE LLRW disposal sites could also be incorporated into such a system.

Ample precedent exists both from a statutory and a practical standpoint for such a plan. High level waste and uranium mill tailings and commercial LLRW are to be disposed of and perpetually licensed under essentially these conditions. Although RCRA section 1006 provides a means to resolve the inherent regulatory conflicts that exist, it is evident that all parties involved in the mixed waste dilemma would be far more comfortable with an explicit Congressional blessing. To justify any such Congressional action the case must be made. Therefore, it is necessary to analyze both the origins of the mixed waste crisis and the merits of deferring to the AEA radioactive waste management system. A preliminary attempt at such an analysis follows.

THE ORIGINS OF MIXED WASTE

The Atomic Energy Act: A Comprehensive System For Nuclear Related Materials

To understand the mixed waste dilemma, it is first necessary to understand the origins of the AEA system for defining and regulating radioactive waste. Contrary to popular opinion, the AEA, not RCRA, was the nation's first "cradle to grave" waste management system, a system that pre-dates RCRA by almost thirty years.

There are two important facets to the AEA regulatory scheme for radioactive materials that have bearing on the mixed waste issue. First, the AEA is deliberately limited to regulation of nuclear materials created by, used in or associated with the nuclear fuel cycle and the utilization of radioactive material for medical or experimental activities. As such, it does not have the scope of a general environmental statute. Second, although its scope is limited, its system for controlling hazards from radioactive materials was envisioned to be both stringent and comprehensive. In enacting the AEA in 1947 and 1954, Congress surely did not ever contemplate that another equally complex system would be simultaneously imposed upon materials falling within the AEA's ambit, since it was intended to provide complete and perpetual public health and safety protection from the potential hazards associated with the unique materials it regulates.

The AEA came into being as a result of the Manhattan project weapons development program and the subsequent creation and growth of the civilian nuclear power industry. As a result and because Naturally Occurring Radioactive Materials (NORM) are ubiquitous in the environment, Congress and the Atomic Energy Commission (AEC), which subsequently split to become NRC and DOE, deliberately limited the scope of AEA regulation to specifically defined nuclear materials. (3)

For example, and in keeping with this notion, Congress and AEC/NRC created a definition of regulated "source material" that excludes natural uranium and thorium ores until they are removed from their place in nature and unless they equal or exceed 0.05% by weight of thorium or uranium. (1) Congress defined the term special nuclear material (used in nuclear weapons) by reference to "uranium enriched in the isotope 233 . . . or 235" (1) and NRC added that such material must be "capable of releasing substantial quantities of atomic energy." (4) Congress also defined the term "spent nuclear fuel" by reference to the nuclear reactor cycle and defied the term high level radioactive waste by reference to "reprocessed spent nuclear fuel." (5) Similarly the definition of "byproduct material" is keyed to either the production and use of special nuclear material or to uranium mining or milling. (1) Finally, both Congress and the NRC defined the term low-level radioactive waste ("LLRW" or "low-level waste" or "LLW") by reference to radioactive materials that either contain, or are themselves, materials subject to AEA regulation, but which are not high-level waste, transuranic waste, spent nuclear fuel or uranium mill tailings. (1, 4)

Thus, the definitions of materials subject to the AEA are narrowly circumscribed. Unlike RCRA, the AEA attempts to be exclusive, rather than inclusive in its approach to determining the materials it regulates and this approach is also reflected in the overall regulatory philosophy of both the AEC and NRC. Moreover, AEA definitions, such as the definition of byproduct material, are inherently process-specific, unlike RCRA definitions, which are based on both characteristics of the waste and/or the processes from which it arises.

Nevertheless, because the AEA represents perhaps the first attempt of environmental policy in the United States to respond to a clearly defined and well documented hazard, that of radioactivity from nuclear material, it goes to great length to ensure complete control over materials falling within its scope. Indeed, in the early days of the AEA/AEC, the entire nuclear industry was created, owned and monopolized by the federal government. (3) The government owned all source material and even today requires a license for its mere possession. Similarly, Congress also made clear that, like no industry before it, the nuclear power industry would be comprehensively regulated from its inception on a cradle-to-grave basis. Id. Moreover, the AEA pre-empted state regulation of radioactive hazards for AEA subject materials. (6) This

comprehensive and pre-emptive authority was implemented through regulations that required the tracking, accounting and regulated disposal of all AEA materials throughout the United States. That system, as originally conceived, was intended to address permanently the hazards from radioactive waste.

Thus, the AEA system was unique in at least two important respects. First, it limited itself narrowly to specifically defined nuclear materials through largely process-specific definitions. Second, for materials falling within its purview it was the most comprehensive system of its time. As RCRA Section 1006 suggests, the 1954 AEA, as amended, never contemplated sharing the stage for regulatory control of nuclear materials with another statute.

The Resource Conservation Act: Mixed Waste Comes Into Being

Because of the pervasive scope of AEA regulation, when Congress enacted the modern version of the Solid Waste Disposal Act in 1976, it took pains to exclude from the definition of solid waste subject to RCRA jurisdiction materials falling under the purview of the AEA.

Thus, under RCRA section 1004 (27), 42 U.S.C. 6903 (27), AEA materials, including source, special nuclear and byproduct material, are excluded from the definition of a solid waste. (8) This exclusion is also carried through into the RCRA implementing regulations issued by EPA at 40 CFR 261.

Furthermore, in enacting RCRA, Congress also made clear that in cases of inconsistency, RCRA would "yield" to other pre-existing programs such as the AEA. According to section 1006 of RCRA:

> Nothing in this act [RCRA] shall be construed to apply to any activity or substance which is subject . . . to the Atomic Energy Act of 1954, except to the extent that such application is not inconsistent with the requirements of such Act. (9)

This language has two equally important effects. First, it appears to contemplate, to the maximum extent practical, a system of dual regulation for materials falling under both RCRA and other statutes. To that extent, it can be viewed as important, although indirect, support for the concept of mixed waste and a complementary AEA/RCRA waste management system. Second, however, it also makes clear that any such system must in fact be complementary, rather than inconsistent, and that in cases of inconsistency, RCRA yields.

Unfortunately however, and as discussed more fully below, RCRA 1006 has never actually been used successfully for this latter purpose. In 1984, DOE, perhaps unwisely, invoked RCRA section 1006 for the proposition that all of its activities falling under purview of the AEA and relating to the nation's national security interests were exempt from regulation under RCRA whether involving RCRA materials or not. (10) Unfortunately, however, DOE lost and the court ruled that RCRA applied to DOE facilities, absent a specific finding of incompatibility. DOE has been criticized for taking this position. In retrospect, had DOE limited its exemption claim solely to AEA regulated materials rather than the entirety of AEA facilities, DOE might have prevailed, thereby largely avoiding the mixed waste issue. According to the court:

> The Court concludes that the most reasonable reconciliation of the RCRA and the AEA is that AEA facilities are subject to RCRA except as to those wastes which are expressly regulated by the AEA: nuclear and radioactive materials.

In the wake of the LEAF v. Hodel decision, Congressional attention was brought to bear on the issue of mixed waste. However, in the 1984 amendments to RCRA, Congress left the status quo intact. Nonetheless, two key members of Congress, Senators John Chafee and Alan Simpson, both of whom were members of the Senate Committee on Environment and Public Works, recognized the importance of the

mixed waste question and issued directly conflicting policy statements regarding mixed waste. According to Senator Chafee:

> The exclusion of Atomic Energy Act materials applies only to the radioactive materials themselves and not to any wastes with which the AEA materials may be associated. RCRA applies to hazardous wastes that are mixed with radioactive materials. Otherwise the mixing of small amounts of radioactive materials with hazardous wastes could transform the entire waste stream into an AEA material exempt from RCRA. (11)

Chafee went on to elaborate upon his view of RCRA section 1006 by noting that:

> Section 1006(a) of RCRA does not in any way exempt mixed hazardous and AEA wastes from RCRA . . . except to the extent that application of RCRA would be inconsistent with specific requirements of the AEA. Thus, only in the rare case where compliance with both RCRA and the requirements of the AEA would be physically impossible are these materials exempt. (12)

Senator Simpson took the opposite view:

> It strains credibility to interpret . . . [RCRA] to mean that the mere presence of hazardous substances in a waste stream that is otherwise primarily made up of source, special nuclear and byproduct material, [subjects such a waste stream to RCRA requirements] since this would have the effect of rendering this particular exemption a nullity . . . [thereby] effectively extend[ing] the requirements of the Solid Waste Disposal Act, as amended, to virtually all radioactive waste streams. (13)

Simpson noted that the language of section 1006, "contemplates more than a demonstration of mere physical impossibility . . . [i]ndeed I can envision a wide range of situations where compliance would not be a "physical impossibility" but would nevertheless be inconsistent with the requirements of the AEA." (13) Simpson went on to include a letter from NRC Chairman Nunzio J. Palladino setting forth numerous incompatibilities between RCRA and the AEA and based largely upon the different approaches taken by NRC and EPA to minimize potential hazards from radioactive and chemically hazardous waste systems. (13)

Unfortunately, the views expressed by Senator Chafee, rather than Senator Simpson, ultimately prevailed at EPA and thus, on July 3, 1986, EPA published a Federal Register notice indicating that states with authorized RCRA programs must apply for permission to regulate the hazardous portion of mixed waste, thereby effectively asserting RCRA jurisdiction over mixed waste. (14) Subsequently, EPA explicitly extended its interpretation of its jurisdiction to include states without authorized RCRA programs--thereby effectively admitting that EPA had not previously regulated mixed waste. (15)
EPA and NRC also issued a Joint Guidance on the Definition of Commercial Low Level Radioactive and Hazardous Waste to all NRC licensees in March of 1987. (16) In this document, EPA and NRC provide a method for identifying low level mixed waste as mixtures of low level radioactive waste and hazardous waste. According to EPA,

> NRC regulations exist to control the byproduct, source and special nuclear material components of mixed LLW; EPA has the authority and continues to control the hazardous component of mixed LLW. However, when the components are combined to become mixed LLW, neither agency has exclusive jurisdiction under federal law. This has led to a situation of dual regulation where both agencies, NRC and EPA, regulate the same waste. (16)

The Paradox Of Dual Mixed Waste Regulation

Although initially appealing, the notion of component-by-component regulation of mixed radioactive and hazardous waste fails to reflect accurately the realities of mixed waste. Indeed this is reflected in EPA's statement that both NRC and EPA "regulate the same waste."

In reality, although it is logically possible to distinguish between hazardous and radioactive components of a waste, in practice, each component is often one and the same. As DOE explained in its final interpretation of its AEA/RCRA responsibilities:

> DOE assumed that the exclusion was intended by the Congress to be applied to radioactive wastes in their real world configuration. Virtually all radioactive waste substances are contained, dissolved or suspended in a nonradioactive medium from which their separation is impractical. Accordingly, DOE noted that in proposing the direct process approach, that unless some radioactive waste streams were considered to be byproduct material in their entirety, RCRA's exclusion of byproduct material might reasonably be perceived to have little effect, because RCRA's application to a nuclear waste's non-radioactive medium would appear to entail at least the indirect regulation of the radionuclides dispersed in the medium. (17,18)

Unfortunately however, and despite DOE's recognition of the basic conflict between joint EPA and NRC/DOE regulation of the same material, DOE's final rule defined AEA byproduct material to refer "only to the actual radionuclides dispersed or suspended in the waste substance." (17,18,19) According to DOE, "the non-radioactive hazardous component of the waste substance will be subject to regulation under the Resource Conservation and Recovery Act." (17,18,19)

DOE's acceptance of a position it had already rejected as impractical exemplifies the "Alice-in-Wonderland" attitude of those involved in the mixed waste dilemma. Taken to its logical extreme, acceptance of DOE's and EPA's interpretation leads to atom-by-atom regulation of mixed waste and, in many key instances, effectively nullifies RCRA's exclusion for source, special nuclear and byproduct material. As one commentator has stated:

> if the phrase "radioactive material" refers only to radionuclides -- the radioactive atoms -- contained in a material, then there is no such thing as a pure byproduct material, except perhaps under controlled laboratory conditions for fleeting periods of time. All material yielded in or made radioactive by any technique will contain at least some nonradioactive atoms and during the passage of time, radioactive decay will gradually increase the ratio of nonradioactive to radioactive atoms . . . . The notion that an individual atom passes from the AEA to RCRA control at the instant of its decay is untenable. (20)

The fact that DOE has endorsed such a view makes clear the degree to which regulators have distorted physical reality as a result of EPA's assertion of RCRA's jurisdiction over mixed waste.

EPA's RCRA rules have only further added to the problem. Under EPA's mixture rule (20), any mixture of a listed hazardous waste and any other material is considered, in its entirety, to be a listed hazardous waste. Thus to the extent that a listed hazardous waste is mixed with any AEA material, the AEA material itself, including the wholly radioactive component, would become a hazardous waste under the mixture rule. In such a case, no distinction at all would exist between the AEA and RCRA portions of the waste as EPA, NRC and DOE guidance have suggested. Recently the United States Court of Appeals for the District of Columbia Circuit invalidated the mixture rule in Shell Oil Co. v. EPA, 950 F.2d. 741 (D.C. Cir. 1991). However, the mixture rule remains temporarily in effect until October 1, 1993, pending EPA's decision whether to repromulgate the rule or abandon it. (22) DOE's rationale for accepting the largely fictitious notion that mixed waste can in significant measure be separated into its hazardous and radioactive components is revealing:

> RCRA is a remedial statute and as such must be liberally construed for the remedial purpose for which it was enacted. The intended comprehensive nature of RCRA's regulatory scheme is evident from the legislative history. The House Committee . . . regarded it as closing the last remaining loophole in the framework of environmental laws . . . Accordingly, DOE decided that RCRA's definitional exclusion of source, special nuclear and byproduct material assumes a narrower significance than was suggested in the proposed rule. (17,18)

The notion of RCRA as a gap-filling environmental statute that was meant to be broadly applied to all situations that are not clearly covered by another statute has played a key role in the creation of the mixed waste quandary. RCRA, drafted in the pro-environmental fever of the 1970's is intended to be a broad statute of general applicability, and EPA's implementation of RCRA has reflected this thrust. In contrast, while the AEA was always intended to be a comprehensive system for regulating specific radioactive materials, both Congress and NRC have always resisted efforts to expand its scope and the mission of NRC beyond these parameters. These differences in approach have allowed EPA to intrude into regulatory areas previously thought to be reserved entirely to NRC under the AEA.

INCONSISTENCY AND INCOMPATIBILITY

NRC's Initial View

The import of RCRA 1006 is that RCRA is to yield in cases of conflict between the AEA and RCRA. Yet EPA, NRC and DOE have interpreted this section narrowly, insisting that it applies only to cases where it is physically impossible to comply with both statutes. In fact, where regulatory requirements with built-in flexibility are involved, it is hard to imagine precisely the exact contours of such a conflict. For instance, although RCRA regulations encourage regular opening and visual inspection of waste containers for sampling and NRC's principle of keeping exposures "as low as reasonably achievable" if read fairly, forbids such practices, the word "reasonably" can be stretched to accommodate such a practice. Yet physically, it is impossible to sample radioactive wastes without increasing exposure unless extreme methods such as robotic sampling are used. Thus, by insisting on "physical impossibility," regulators have committed themselves to the unenviable task of continually attempting to reconcile fundamentally inconsistent regulatory systems.

As discussed more fully below, many obvious inconsistencies have been identified from the outset of the mixed waste debate. In 1984, NRC made the following statement to Congress:

> We believe regulation by EPA under RCRA of radioactively contaminated chemical wastes currently under NRC and agreement state jurisdiction is inconsistent with our regulatory requirements established pursuant to the Atomic Energy Act. Radioactively contaminated chemical wastes regulated by NRC and agreement states should not be regulated under RCRA. (23)

Unfortunately, little heed has been paid to this statement.

The NRC/AEA Radioactive Waste Management System

Radioactive waste and chemically hazardous waste are quite simply not the same. Systems for managing and permanently disposing of each type of waste differ in significant respects. The basic difference between radioactive and chemically hazardous waste is that the hazard from radioactive waste can only be eliminated by time and transmutation; it is not possible to effectively eliminate the hazards from radioactive waste by treatment or solidification alone. As NRC has noted, "because the hazard posed by low-level waste is of an atomic nature, its hazard is inherent, i.e., independent of its chemically bound state. Destruction of the LLW hazard, aside from transmutation processes, is impossible." (24) Moreover, unlike chemical hazards

which are often perceptible to human senses, radiation can neither be seen, smelled nor felt. While in many cases hazardous waste can actually be destroyed by processes such as incineration, it is not possible to destroy radionuclides. (24)

The need for long-term management of LLRW is the primary influence on NRC's Part 61 radioactive waste disposal system. As NRC Chairman Palladino noted to Congress in 1984,

> NRC has emphasized a systems approach to low-level waste disposal including consideration of site selection, site design and operation, waste form and disposal facility closure. In addition to focusing on disposal site performance, NRC has specified a number of requirements which must be accomplished by the waste generator, including requirements for waste form and content, waste classification and waste manifests. (23)

Because of the unique hazards associated with exposure to radioactive activity and the fact that radioactive waste may remain hazardous for hundreds of years, NRC's approach uses "passive" rather than "active" systems to minimize and retard releases to the environment over the extremely long time frames contemplated for control of radioactive material. NRC's system uses a performance objectives approach by which control of hazards posed by chemical wastes (that may be equally as long-lived as radioactive hazards) is subsumed under the long-term hazard minimization framework for radioactive wastes.

AEA systems are designed permanently to isolate the waste from virtually all human contact. This is achieved through use of institutional controls such as government site ownership, site security measures and permanent monuments to prevent intrusion into the waste site. Isolation of the waste in the disposal unit is achieved through "natural materials," such as clay liners and covers or engineered surface barriers, that can last for long periods of time and permanently minimize contact of the radioactive waste with water.

NRC performance objectives assume that there will be no "active" controls at the site after 100 years and that depending on the waste classification the site must be designed to last up to 300 to 500 years. (25) Engineered intruder barriers are designed to prevent entry into the disposal unit even if "institutional memory" is lost at the site over the 300-500 year period following initial disposal. In order to minimize the potential for such loss of "institutional memory," a state or federal government is expected to own the site in perpetuity. (26) NRC sites use the surrounding site as a means of retarding releases to the environment; thus the site itself, including the subsurface zones, is considered part of the containment mechanism and the disposal unit is designed such that acceptably small quantities of radioactivity are released into the surrounding environment over time. (27)

By contrast, the RCRA "minimum technology" standards expressly require disposal units to be equipped with dual synthetic liners and leachate collection systems. (28) Regular and frequent groundwater and leachate sampling, monitoring and analysis are conducted in order to confirm constantly the status and location of the waste. (29) RCRA standards contemplate normal time frames of approximately 30 years and rely on the above-noted "active" controls to isolate the waste from any contact with the site or the surrounding environment. Releases to any part of the environment are prohibited and prompt action to correct such releases are required. (29) Indeed, some state laws for hazardous substances set release limits at detection levels without regard to any estimated risk to human health or the environment. The AEA disposal scheme cannot truly be reconciled with such a system. After 30 years, the site may be sold. (30) These two regulatory methodologies are fundamentally inconsistent. For example, although it is physically possible to install a synthetic liner and leachate collection system in an AEA type disposal unit, NRC has consistently maintained that a synthetic liner will prevent any infiltrating rainwater from escaping the disposal unit, hence in order to prevent the unit from filling up like a bathtub, active leachate collection and pumping is continually necessary. Yet, there is a strong possibility that over hundreds of years, pumping may be discontinued, thereby leaving open the possibility that the unit will actually overflow, resulting in exactly the type of sudden, catastrophic release that the AEA system is designed to prevent. Furthermore,

even if it is possible to continue pumping over such a long time period, pumping of radioactive leachate creates additional human exposure to radioactivity in violation of NRC's long-adhered-to principle of maintaining exposures as low as reasonably achievable ("ALARA").

Active pumping of leachate creates an additional disposal problem by potentially generating more radioactive mixed waste in liquid form, thereby further violating ALARA. Moreover, under RCRA's mixture rule, leachate containing listed wastes may carry listed waste codes for all listed wastes disposed in the landfill, thereby further complicating and obstructing treatment and disposal solutions. Finally, because radioactive contamination occurs simply through contact with radioactive substances, treatment and packaging of radioactive waste can contaminate treatment and packaging facilities and equipment -- thereby generating additional radioactive waste.

Although performance characteristics of synthetic liners used for longer than 50 years are not well known, no one suggests that they may be effective for hundreds of years. DOE has noted that "synthetic materials incorporated into RCRA sites probably will not last for 200 to 1,000 years." (27) Synthetic liners will "drain out" eventually from gravity or fail because of subsoil settlement, puncture by rocks, splitting seams or entrapped air bubbles. (31) This fact is also acknowledged by EPA: "eventually, liners will either degrade, tear or crack and allow liquids to migrate . . . it is therefore important that liquids be removed during the time a liner is most effective. (32) Finally when a synthetic liner ultimately does rupture, unlike a clay liner, it is not self-healing. (31) Thus, synthetic liners pose the potential for more concentrated discharges of contamination by funneling all liquids in the landfill to the point where a liner is breached. Finally, use of a synthetic liner may cause moisture retention in waste materials and, as a result of slower dehydration, cause differential settlement or cracking of both clay caps and liners, thereby leading to either additional infiltration or exfiltration of moisture.

Nor are the conflicts limited to liners. EPA recently stated "synthetic covers also have a limited life, especially in dry, sunny, windy areas." (37) Furthermore, NRC controls are designed to eliminate any potential for intrusion into disposal units. Standpipes and leachate collection systems however are designed to provide exactly such access. Furthermore, state or federal site ownership, which is required at NRC disposal sites, can raise serious questions of site liability under hazardous waste statutes such as RCRA and CERCLA. At the Envirocare of Utah, Inc. site in Utah, where mixed waste is being disposed, the state of Utah flatly refused to accept site ownership based on RCRA- and CERCLA-type liability concerns, thereby forcing the State Division of Radiation to waive the site ownership requirement specifically for the Envirocare site.

NRC and Congress have been aware of the differences between the AEA and RCRA final disposal approaches for nearly a decade. As NRC noted in 1984:

> the regulatory system embodied in 10 CFR pt. 61, including generator responsibility, and reliance on packing, waste stabilization and site characteristics, provides a more effective long-term approach to minimizing the formation and migration of leachate from radioactive waste than a policy that relies heavily on the use of liners in burial trenches. EPA itself recognized the limitations of liners in its standards that . . . only [require] liners [to] prevent migration during the "active life" and subsequent closure of the landfill . . . . EPA's approach may well be appropriate for . . . chemical wastes . . . [however] for burial of low level radioactive waste . . . we do not believe that liners will totally eliminate the potential for groundwater contamination . . . [and] we have concerns that liners will contribute to the accumulation of leachate, which will fill up the disposal unit and possibly overflow. Removal and treatment of this leachate will almost certainly involve a release of some of the contaminants to the environment. (23)

In spite of NRC's concerns regarding the incompatibility of using liners within the AEA system, in 1987, NRC and EPA released a Joint Guidance on a Conceptual Design Approach for Commercial Mixed Low-

Level Radioactive and Hazardous Waste Disposal Facilities. (34) According to EPA and NRC, the design concept set forth in the guidance "demonstrate[s] the integration of EPA's regulatory requirements for two or more liners and a leachate collection system . . . and the requirements of the AEA that require the contact of water with the waste to be minimized." (34) The design calls for an above-ground disposal unit with run-on controls, dual synthetic liners, a clay liner, and a leachate collection system. (34) Such a unit would be capped by either a clay cap or an engineered vault with a clay cap. (34) However, both EPA and NRC were careful to state that "the concepts proposed . . . are presented as general guidance . . . this guidance will not affect the requirements for waste disposal facilities to comply with all applicable NRC and EPA regulations." (34)

No facility meeting the design concept described above has yet been built. Although mixed waste is being land disposed at the Envirocare of Utah, Inc. facility in Clive, Utah, the Envirocare disposal unit does not meet the joint NRC/EPA design criteria. Moreover, questions continue to arise regarding the suitability of synthetic liners for disposal units containing radioactive waste. For instance, in 1990, NRC State Programs Director, Carleton J. Kammerer, wrote to the California Department of Health Services regarding EPA Region IX's recommendation that California's proposed low-level radioactive waste facility use a synthetic liner. NRC's clear conclusion is that such an approach is ill-advised for a host of reasons. For instance,

> incorporating a liner and leachate collection system . . . would require the applicant to demonstrate that the performance objectives would not be violated over the long-term (e.g., 500 years or more) as a result of water accumulation within the disposal trenches. Such a demonstration could be difficult since water accumulation could theoretically result in a continuing need to pump and treat the leachate, in direct discharge of contaminated leachate to the land surface, or in a concentrated discharge of leachate to the vadose zone when the liner failed.

Although NRC staff has stated that a double liner and leachate collection system might offer "enhanced groundwater protection," it also noted that such protection might only be temporary.
Other reasons cited by NRC for its recommendation against the use of a liner include questions regarding long-term liner stability and the increased potential for rainfall infiltration caused by the use of synthetic liners. Furthermore, NRC specifically declined to endorse without qualification the Joint EPA/NRC Guidance On a Conceptual Design Approach For a Mixed Waste Facility. NRC noted that:

> It is important to recognize that the [Joint NRC/EPA] guidance presents a conceptual design only; any application adopting this design approach would have to demonstrate . . . that the disposal system does not suffer from the same limitations and potential problems described above for disposal units that include liners and leachate collection systems. (34)

In light of NRC's other comments regarding liners outlined above, it is difficult to see how such a demonstration could actually be made. (35)

In fact, a study conducted by DOE in 1987 concluded that an above-ground vault constructed in accordance with the NRC/EPA Joint Guidance would result in a peak dose of radionuclides approximately one order of the magnitude higher than traditional AEA below-ground disposal units and would not meet the requirements of 10 CFR pt. 61 for maximum effective dose limits. (36) Moreover, as DOE has noted, in the context of requiring RCRA-type controls at uranium mill tailings sites:

> Longevity requirements have led to disposal designs that use only natural materials and that incorporate (or consider) the subsurface zone as an integral part of the natural disposal system. . . . The differences between RCRA sites and UMTRA project sites reflect different technological choices. . .these different technological choices. . .have led to what the DOE believes are conflicting and mutually inconsistent requirements with respect to implementing longevity requirements and the meeting of proposed groundwater standards [for UMTRA sites], only natural material and systems have

the properties and characteristics essential to such a design life. (27)

Furthermore, DOE also notes that RCRA systems requiring leachate collection will be extremely difficult to reconcile with NRC's passive systems approach. According to DOE:

> it would be necessary to relax the UMTRA project requirements for minimum post closure maintenance before the concept of integrating the leachate for treatment can be applied on the UMTRA project. It can be argued that [if] UMTRA project wastes were placed on very low permeability liners and provided with underdrains or leachate collection systems, the leachate could be brought to evaporation ponds that could operate with minimum or no human intervention. To prevent inadvertent human access to the leachate, the leachate could drain into rock-filled, lined sumps or toe aprons. . . . However, it may be difficult to argue that such an approach could protect the environment and ensure human health and safety for periods extending to 1,000 years. (27)

Thus, not only is it the case that the joint NRC/EPA design concept may result in higher exposures than a traditional radioactive waste disposal unit, but more importantly, with synthetic materials and active leachate collection, the long-term passive control necessary over the extremely long radioactive waste control time frames may not be possible. As it stands then, the EPA/NRC Joint Guidance remains unproven and provides a good example of an attempt by NRC and EPA to mask an obvious incompatibility between the AEA and RCRA requirements identified by DOE.

RCRA And Incompatibility: The Land Ban

From a RCRA perspective, there are equally, if not more dramatic inconsistencies. Perhaps the most compelling of these is the application of the RCRA land disposal restriction ("LDRs") to mixed waste. Under the LDRs, the land management of certain untreated hazardous wastes is prohibited. This prohibition includes both the storage and disposal of untreated waste without a permit. (35)

Because treatment and disposal capacity for many mixed wastes is extremely limited and because the presence of radioactivity further complicates treatment solutions for mixed waste, especially where the required treatment is incineration, EPA has been forced to grant a "national capacity variance" for DOE's mixed wastes. (37, 38) Yet even this variance has already begun to expire and all such variances will end by mid-1994. (38) For instance, in 1990, EPA granted a national capacity variance for so-called "third third" mixed wastes; this variance expired in 1992. (38) Although DOE has applied for an extension, EPA has not yet granted it. In any event, under the statute it can only be renewed until May of 1994. (39)

In the meantime, although DOE has identified acceptable treatment technologies for approximately 75% of the volume of its mixed waste streams, treatment "capability" for the remaining 25% does not yet exist and is hampered by a lack of technologies capable of properly managing the radioactive component of the waste. (39) Even assuming that such treatment capability exists, treatment capacity for mixed waste is extremely limited for both DOE wastes and commercial mixed wastes. (39) Construction of future treatment capacity is estimated by DOE to take between 5 and 15 years. (39) Similarly, disposal capacity for mixed wastes is also extremely limited. (39) The extreme difficulty of obtaining a RCRA permit, particularly for incinerators and landfills, further complicates the picture.

Thus, the mixed waste dilemma has been described as a situation in which "EPA and the state authorities, via RCRA and the LDRs, are in the position of requiring DOE and the other mixed waste generators to do something that everyone acknowledges is impossible and then makes the same generators subject to fines and penalties for not doing the impossible." (38)

As a result, it is evident that for the foreseeable future, DOE will continue to violate the RCRA LDR's. (38) In recognition of this fact, Congress passed the Federal Facilities Compliance Act of 1992. (39)

Under this Act, Congress was forced to revoke expressly the waiver of sovereign immunity under section 6001 of RCRA as it applies to DOE's compliance with the LDR's for mixed waste. (39) DOE thus has three years to bring itself into compliance with LDR requirements. After that time, DOE may still fail to meet the LDR standards but must meet other requirements under the FFCA. (39) Thus, although technically, the mixed waste situation has resulted in DOE being in continuous violation of RCRA, Congress has decided that DOE will not be subject to fines or enforcement for at least another three years. (39) EPA, in turn, has also indicated via its RCRA enforcement policy, that mixed waste will be placed low on EPA's list of enforcement priorities.

The RCRA LDR situation presents a clear example of the absurdity of the current mixed waste treatment and disposal system. Application of RCRA to mixed waste has resulted in an ongoing violation of RCRA itself that can only be cured by an act of Congress. EPA has therefore been forced to ascribe a low enforcement priority for mixed waste-related RCRA violations. Ironically, in this case RCRA has been forced to yield, albeit temporarily, consistent with the spirit of RCRA 1006. Yet while DOE, EPA and NRC remain hopeful that the situation can be resolved through the development and construction of more existing and innovative treatment capacity, such developments clearly will not take place by the end of 1994. Even if sufficient treatment capacity becomes available, all mixed waste generators and storers will still face the root problem of lack of disposal capacity meeting both RCRA and AEA requirements.

The Importance Of Waste Form

Another essential and basic difference between NRC and EPA final disposal requirements is the importance of waste form in the NRC scheme. Although initially NRC, like EPA, focused most strongly on the disposal unit itself, as opposed to the form of the waste disposed, NRC ultimately recognized that the form of the waste was equally important. (40,41) Thus, as the Congressional Office of Technology Assessment ("OTA") has noted, "NRC LLW regulations are based on the stability of the waste and the stability of the disposal site." (42)

Thus, the NRC standards require all Class B and C low-level radioactive wastes to meet structural stability requirements and Class A wastes to be processed, as appropriate, to remove free liquids. Requirements for Class B and C wastes can be strict enough to require encasing wastes in high integrity containers such as stainless steel and concrete. (43) The waste form standards are designed to ensure that the waste does not degrade or subside within the disposal unit. Id. Structural stability is also required in order to provide greater protection against exposure to an inadvertent intruder. (43) NRC requirements include standards for testing of waste form in accordance with leaching, compression, thermal cycling and biodegration parameters. (43) Because NRC's emphasis is on the entire disposal systems' performance, which must provide long-term stability without active controls, disposal trench stability is achieved in large part by waste forms meeting long-term stability requirements. (24)

By contrast, RCRA does not specifically include waste form requirements and emphasizes the overall ability of the disposal unit to completely isolate wastes, regardless of their form, from any contact with the environment. Although EPA regulations prohibit the addition of liquids to landfills and place restrictions designed to eliminate subsidence on waste form, unlike the NRC standards, they rely less heavily upon waste form as an integral part of the overall containment method. Thus, while liners and leachate collection systems may be necessary for RCRA wastes disposed under relatively lenient waste form requirements, for wastes meeting NRC waste form requirements, such controls may not be necessary and may actually be harmful.

By volume, the largest non-DOE category of mixed waste is low-level mixed wastes containing organic solvents and scintillation media such as toluene and xylene. (44) The organic solvents in these wastes are precisely the types of constituents that present the chemical hazards the RCRA program is designed to eliminate through controls on leaching and migration. Although the great majority of this waste is suitable

for incineration without regard to its radioactive content, in the past, some of these wastes were in fact disposed at existing LLRW land disposal sites. Interestingly enough, this disposal does not appear to have resulted in significant chemically hazardous environmental contamination. It is worth noting that waste that is considered "absorbed" under the NRC system would be considered "solidified" by the chemically hazardous waste handling community. Indeed, an analysis conducted in 1985 by NRC suggests that mixed waste that is solidified or absorbed (48) in accordance with NRC's waste form requirements at 10 CFR 61.56 is unlikely to leach and be released from wastes buried in a part 61 facility:

> Water (including or carrying with it acquired materials) is assumed to be the principal leachate to which wastes will be exposed (it should be noted that a large part of the rationale behind the required NRC Class B and C waste stabilization in 10 CFR Part 61 was based on minimization of contact of waste packages with water). Dissolution of organics in water is unlikely as the mechanism of removal (based on the concept of chemical dissimilarity and immiscibility of aqueous and organic phases); this is further substantiated by the documented ability of many absorbents to retain sorbed organics in the presence of, or even surrounded completely by, water.
>
> In summary, removal of sorbed organics should be considered from the point of view of being caused by thermal gradients, pressure, agitation or vibration, leaching by "pure" water, and water containing acquired components. It is not clear whether thermal or pressure forces can effect removal of these materials but, in any event, for the removal to occur, the conditions must be different (and, most likely more severe, i.e., higher temperature and pressure) from those under which the sorption process originally occurred. It is not likely that higher temperatures would be encountered by sorbed wastes for significant periods of time and certainly not at all after burial. (46).

Thus, NRC waste form requirements may well provide significant protection against the migration of chemical (as well as radiological) hazards, thereby further calling into question the need for dual EPA/NRC regulation of mixed wastes containing significant amounts of radioactivity.

Other Inconsistencies

Other key inconsistencies between RCRA and AEA requirements include the fact that RCRA's and EPA's implementing regulations encourage and require extensive sampling and manual inspection of waste in order to characterize the material. (45) Under NRC guidelines, radiation waste storage requirements are designed to minimize and discourage human access to the waste since radiation cannot be perceived by human senses and can have potential effects long after exposure. Furthermore, RCRA wastes are generally more uniform then AEA wastes and thus can be more effectively characterized through sampling. Because of these differences, compliance with EPA RCRA standards could lead to increased public or occupational exposure of workers to potentially dangerous radioactivity. A report by the Nuclear Power Industry notes that EPA requires a 100 gram sample for testing that could increase worker radiation exposure and the need for visual inspection under RCRA could also increase such exposure. (46)

Although NRC and EPA have recently released a Draft Guidance: Clarification of RCRA Testing Requirements for Mixed Waste (March 1992), which acknowledges these problems, EPA attempts to resolve the difficulty by simply noting that: "A combination of common sense, modified sampling procedures and cooperation among regulatory agencies will minimize any hazard associated with sampling and testing mixed waste. (46) Unfortunately, EPA fails to provide any support for this convenient conclusion and EPA's track record on mixed waste fails to provide such evidence of either genuine cooperation or significant common sense.

NRC and EPA regulations also often require duplicative reporting and paperwork requirements. Both NRC and EPA require a comprehensive manifest and record keeping system. They also require strict security protections that are not always identical, and both NRC and EPA have financial assurance requirements,

which can force site operators to commit large sums of money to NRC and EPA for essentially the same purposes.

Dual Regulatory Regimes: A Lack Of Corresponding Benefit

The inconsistencies caused by joint EPA, NRC and DOE regulation of mixed waste are readily apparent. As RCRA becomes increasingly stringent and complex, these inconsistencies can only multiply. Although NRC, EPA and DOE have repeatedly insisted in their official regulatory policies that these conflicts can be reconciled, they have not been and likely cannot be reconciled.
In 1990, NRC Commissioner James Curtiss asked the NRC Advisory Committee on Nuclear Waste ("ACNW") to compare NRC's and EPA's disposal requirements for mixed waste. In response, ACNW identified a number of "fundamental differences between the requirements of the two agencies." (47) These differences included the use of synthetic versus clay liners, the use of active versus passive systems, differences in packaging and treatment of radioactive wastes, differences in disposal time frames (i.e., 30 v. 500 years) and the rapidly evolving nature of RCRA requirements versus the more stable AEA standards. (47) Moreover, ACNW also noted that while "staff members of the EPA and NRC have been attempting for some time to develop an approach through which dual regulation could be made more practicable . . . the efficacy of these [EPA/NRC] joint guidance reports is not entirely clear." (47) According to ACNW, "discussions with state representatives indicate that additional guidance is necessary . . . [and the joint guidance reports] do not alleviate the dual regulation burden." (47) Thus, as is evident, EPA's and NRC's attempts to paper over the conflicts caused by the dual regulatory regime have generally not been successful.

It is important to understand that the EPA and NRC regulatory frameworks are configured differently. EPA's RCRA regulations are prescriptive and extremely complex in nature, frequently imposing extraordinarily precise standards and methods and even specifying particular materials. NRC regulations, on the other hand, appear less complex and less prescriptive. Their focus is oriented more toward overall and long-term system performance. However, NRC's regulations are supported by a large body of NRC Regulatory Guides and Technical Position Papers that lay out in detail methods or requirements that are acceptable to NRC to meet the regulations' performance goal. Although alternatives may be proposed by licensees, the end result of the requirements ultimately imposed by NRC also end up being extremely prescriptive.

In some respects, these differences make sense when one considers that while EPA must permit and license hundreds and even thousands of hazardous waste sites, the number of NRC sites, particularly new sites, is significantly smaller (approximately 7,500), thereby affording NRC the opportunity to scrutinize more carefully individual licensing decisions. The level of detail actually found in the NRC regulations might lead one to conclude that NRC regulations are generally less stringent, thereby in turn leading one to conclude erroneously that the more prescriptive EPA regulations can be imposed without conflict and will result in an additional level of protection. In reality, this is not the case.

NRC standards are designed to protect against potential public health and safety threats for time frames that are several orders of magnitude longer than the RCRA standards. By necessity, NRC site selection parameters are more stringent. NRC waste form requirements are more integral to the NRC program and are significantly more stringent than relevant EPA standards. As NRC has noted, "overall the part 61 regulatory system provides a more effective, long-term approach to minimizing formation of leachate from radioactive wastes than a policy that relies heavily on liners." (23)

Both DOE and the Nuclear Management and Resources Council, Inc. ("NUMARC"), have also indicated that the NRC regulatory scheme may provide protection against public exposure to radioactive waste that is superior to that of a joint AEA/RCRA facility. (46,35)

> Projected long-term performance of the [RCRA] 40 CFR 264 facility . . . may be inferior to that of

> the 10 CFR 61 facility assuming mixed waste commingled with LLW is disposed at the latter . . . the effect of imposing 40 CFR 264 requirements on disposal of mixed waste may be to increase the potential individual doses from what they would have been had the waste been disposed as low-level radioactive waste without regard to its hazardous content. (1,35,48)

A recent study of tank requirements under the AEA and RCRA reached a similar conclusion regarding hazardous waste/radioactive waste tanks. (49)

EPA's scientific basis for asserting RCRA jurisdiction over many mixed waste streams is quite thin. There is little, if any, evidence to suggest that prior to RCRA, the AEA failed to account properly for and control both the radioactive and the chemically hazardous component of AEA regulated waste. For instance, one of the most frequently encountered mixed wastes at AEA sites is scintillation vials containing toluene. The risk of potential off-site groundwater contamination from toluene is often used to justify dual mixed waste regulation. Yet a study conducted by NRC in 1986 noted that "toluene has previously been detected in groundwater from trench sump samples at Barnwell and other sites, but concentrations decrease over short time periods indicating a relatively brief persistence in groundwater." (1,35,48) Thus, it does not appear that toluene, known to be disposed of at existing LLRW sites, has actually presented a significant environmental hazard. (24)

In fact, NRC's study of nonradiological groundwater quality at existing low-level waste sites provides a strong indication that there is little reason to be concerned about the impact on off-site groundwater of chemically hazardous constituents found in LLRW disposed in AEA regulated facilities. According to NRC, at the Sheffield, Illinois site, where significant amounts of chemically hazardous low-level wastes are known to be disposed, "the sample results do not indicate that contamination from toluene and xylene scintillation liquids, chromate wastes or lead is occurring . . . ." (48) These wastes comprise the largest volume of known mixed wastes. (44) Moreover it is worth noting that in significant respects, the closed Sheffield site was actually less stringently controlled than a current site regulated under 10 CFR 61, primarily because of Part 61's waste classification system and related waste form requirements.

At the Barnwell, South Carolina site, which NRC stated does essentially meet 10 CFR part 61 requirements, NRC reached the same conclusion: "the LLW disposal units have had a very minor effect on the nonradiological quality of on-site groundwater . . . concentrations of individual organics are very low in on-site wells and are below detection at boundary wells." (48) Thus, the best available evidence suggests that EPA's concerns regarding substantial groundwater contamination from mixed waste at LLRW disposal sites are misguided.

As these examples demonstrate, the principal hazard from mixed waste that is to be land disposed is from the long-term radioactive hazard, not from chemical constituents. The mixed waste regulatory system should, but does not, reflect this fact. In reality, the mixed waste regulatory system arises from the failure of regulators to acknowledge the unique properties of radioactive wastes and to affirm the fact that for such wastes, RCRA and the AEA cannot be reconciled. The failure to recognize this point has led to a multitude of conflicting guidance, statements, and policies aimed at reducing the appearance of conflict. Thus far, EPA and NRC have issued the following joint guidance: Guidance on the Definition and Identification of Commercial Mixed Low-Level Radioactive and Hazardous Waste and Answers to Anticipated Questions (January 8, 1987); Combined NRC-EPA Siting Guidelines for Disposal of Commercial Mixed Low-Level Radioactive and Hazardous Waste (Directive Number 9480.00-14, June 29, 1987); Joint NRC-EPA Guidance on a Conceptual Design Approach for Commercial Mixed Low-Level Radioactive and Hazardous Waste Disposal Facilities (Directive Number 9487.00-8, August 3, 1987); Low-Level Mixed Waste, A RCRA Perspective for NRC Licensees (EPA/530-SW-90-057. August 1990); Memo to All NRC Licensees: Guidance on the Land Disposal Restrictions' Effects on Storage and Disposal of Commercial Mixed Waste (Directive Number 9555.00-01, September 28, 1990). It has spawned an entire generation of environmental professionals seeking to develop treatment technologies that are intended to solve by physical means what

is essentially a legal infirmity.

In point of fact, the only two credible reasons for imposing RCRA requirements on non-treatable AEA regulated wastes -- to enhance groundwater protection and alleviate concerns regarding impermissible mixing of hazardous and radioactive wastes -- are easily dealt with in ways that avoid forcing mixed waste generators to run the imposing gauntlet of full-blown RCRA requirements. EPA's RCRA rules already prohibit impermissible dilution and mixing of hazardous wastes (50) and could easily be modified to provide additional protection. In addition, ACNW has concluded that "the disposal of mixed wastes can be accomplished under the umbrella of NRC requirements for low-level wastes if these requirements are modified to provide for enhanced groundwater protection." (47)

A PROPOSED SOLUTION

The Status Of Uranium Mill Tailings

The illogic of imposing RCRA on low-level radioactive wastes posing significant radioactive hazards is perhaps best seen by comparing the status of mixed waste with an AEA counterpart, uranium mill tailings. Although many uranium mill tailings piles are composed of radioactive waste containing significant amounts of chemically hazardous components, including acids, solvents, and heavy metals, they do not fall within the scope of the mixed waste system and EPA's RCRA requirements. This disparity of treatment derives mainly from the language of Section 11e(2) of the AEA.

Section 11e(1) of the AEA, 42 U.S.C. 2014e(1), defines the term byproduct material, which encompasses low-level radioactive waste, as "any radioactive material yielded in or made radioactive by exposure to the process of producing or utilizing special nuclear material." (1) By contrast, section 11e(2) defines uranium mill tailings byproduct material as "the tailings or wastes produced by the extraction of uranium or thorium from any ore processed primarily for its source material content." (1) Thus, while the 11e(1) definition applies only to radioactive materials, the 11e(2) definition applies not only to radioactive tailings but also to any wastes produced by the extraction or concentration of uranium or thorium. This small difference in wording has meant that under RCRA's exclusion for byproduct material, 11e(1) byproduct material falls within the purview of the mixed waste system, while 11e(2) material does not. In an NRC Memorandum from Paul Lohaus to all NRC Uranium Recovery Licensees, dated March 5, 1989, noting that all 11e(2) wastes, including nonradioactive ore residues and process fluids are byproduct material falling outside the definition of solid waste. (51) Note, however, that the addition of hazardous waste to 11e(2) material after and outside the uranium or thorium extraction and concentration process would cause the material to become a mixed waste. Because of this fact, DOE and NRC have made clear to owners and operators of uranium mill tailings piles that they should take care to prevent the addition of hazardous waste and materials containing hazardous wastes into 11e(2) tailings piles. (17,51). In many instances 11e(1) and 11e(2) byproduct materials may be virtually identical, physically, chemically, and radiologically. A U.S. NRC, SEC'Y Document of Aug. 7, 1991 notes that many bulk non-11e(2) wastes are similar enough to mill tailings to be disposed in mill tailings piles. (52) The fact that physically identical materials presenting essentially identical potential radiological hazards can be subject to such disparate regulatory requirements points out the overall absurdity of the current mixed waste legal framework.

The legal framework created by Congress for uranium mill tailings sites is worth examining for its potential applicability to the mixed waste context. Under the Reorganization Plan No. 3 of 1970, 5 U.S.C. App. 1133, EPA acquired the AEC's authority to promulgate "generally applicable environmental standards" including "limits on the radiation exposures . . . in the general environment outside the boundaries of locations under the control of persons possessing or using radioactive material." (51) The AEC (and later the NRC) retained exclusive responsibility for the implementation and enforcement of on-site radioactive standards through its licensing authority. Thus, under this plan, EPA was to promulgate standards that

would protect against off-site releases of radioactive materials and the AEC/NRC would regulate on-site activities in accordance with these requirements and its own responsibilities under the AEA.

In 1981, Congress used essentially the same framework for uranium mill tailings under the Uranium Mill Tailings Radiation Control Act ("UMTRCA"). (53) Under UMTRCA, all uranium mill tailings are disposed of on land owned or to be owned by a state or DOE in perpetuity. (53) At inactive uranium mill tailings sites, described in Title I of UMTRCA, DOE owns and regulates the site until closure, at which time the site is licensed in perpetuity by NRC. NRC reviews DOE's site closure plan to determine if it will meet NRC's perpetual licensing requirements.

At active sites, falling under Title II of UMTRCA, a private operator is licensed by NRC until closure. (53) At closure, DOE or a state becomes the site owner. Thereafter, the site is licensed in perpetuity by NRC. (1)

Under UMTRCA, and using essentially the same language as it did in the 1970 Reorganization Plan, Congress imposed on both active and inactive uranium mill tailings sites "generally applicable" EPA standards "for the protection of public health and safety from both radiological and non-radiological hazards." (1) Congress decreed that these standards "shall, to the maximum extent practicable, be consistent with the requirements of the Solid Waste Disposal Act." (1) In addition, Congress specifically noted that for active sites, "no permit is required under the Solid Waste Disposal Act." (54) Thus, at active uranium mill tailings sites, NRC licenses the sites in accordance with its own regulations found at 10 CFR pt. 40, Appendix A. NRC's licensing of the sites must conform to EPA's "generally applicable" standards found at 40 CFR pt. 192. (1)

Given the identity of language used in both the Reorganization Plan and in UMTRCA for "generally applicable" standards, it was plain that Congress intended for the EPA part 192 regulations to provide protection only for off-site release at mill tailings sites, especially given the fact that AEA licensed tailings piles, like 10 CFR pt. 61 sites, expressly contemplate and use on-site releases as part of the containment mechanism. Unfortunately, however, in AMC v. Thomas, the United States Court of Appeals for the Tenth Circuit held that EPA could promulgate "generally applicable" standards that have on-site effects. (55) Thus, as a result of that decision the current legal framework for uranium mill tailings piles is flawed in one important respect. It nonetheless provides an important model for use in the mixed waste context. As a practical matter, significant regulatory conflicts between the AEA and RCRA systems have been limited under the UMTRCA system.

The High Level Waste Legal Framework

The concept of NRC licensing DOE in perpetuity at a DOE owned and operated site was also used by Congress in creating a regulatory framework for high level waste. Under the Nuclear Waste Policy Act, DOE is responsible for selecting and establishing permanent disposal facilities. (5) Generators and owners of high level waste are to contribute to a fund to pay for DOE's costs. (5) DOE is to be licensed at the site by NRC. (5) EPA is to promulgate "generally applicable standards for protection of the general environment from off-site releases from radioactive materials." (5) These standards are found at 40 CFR pt. 191. NRC implements these standards through its licensing authority.

EPA's proposed part 191 standards are designed to protect against off-site releases but are also designed to be consistent with the overall design concept of the high level waste repository. In particular, like other radioactive waste disposal sites, the high level waste sites will use the area within the disposal unit as part of the containment structure. As noted in the House Report for the Nuclear Waste Policy Act, "the primary feature of the site . . . consists of a rock medium about 1,000 feet or more underground that will provide one of the primary containments of the waste." EPA's proposed standards are consistent with this approach and contain standards allowing limited releases to the accessible environment over a 10,000 year period.

(54)
According to the standards, and consistent with NRC's long-term approach toward radioactive waste, the "performance assessments [for calculating releases] need not provide complete assurance that the requirements of 191.13(a) will be met. Because of the long time periods involved . . . there will inevitably be substantial uncertainties in projecting disposal system performance. Proof of . . . future performance is not to be had in the ordinary sense of the word in situations that deal with much shorter time frames, what is required is a reasonable expectation . . . that compliance with [40 CFR] 191.13(a) will be achieved." (5, 56)

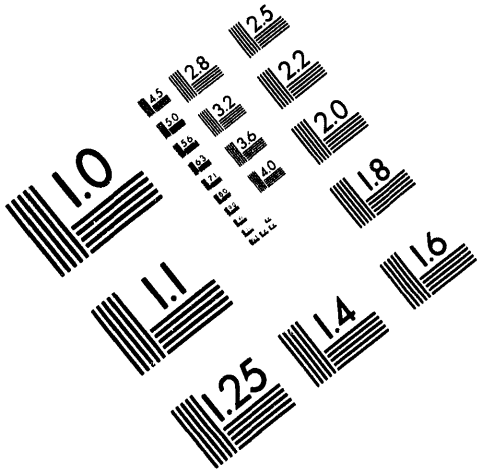
Thus, the proposed EPA high level waste standards recognize the very different and long-term nature of radioactive waste and work within the NRC framework. In accordance with this fact, NRC's licensing of the high level site to be managed by DOE must be consistent with the EPA standards. (5)

A Solution To The Mixed Waste Dilemma

The example of high level waste provides an excellent model of a legal framework in which NRC has lead authority in licensing DOE for a radioactive waste site pursuant to and consistent with EPA's requirements for the protection of the general environment from off-site releases. There is no good reason why a similar legal framework could not be applied to all mixed wastes that contain more than de minimus amounts of radioactivity in the United States, for both DOE and commercial mixed wastes. Disposal of mixed waste (including the relatively small volumes of commercial mixed waste) could take place either at DOE owned and operated disposal sites licensed in perpetuity by NRC or at privately operated commercial LLRW sites (such as the existing Compact sites) on land owned (or to be owned) by a state or DOE and subject to perpetual licensing by NRC. These sites would be subject to a single set of NRC standards that could be drafted to include enhanced groundwater protection and to conform to EPA standards of general applicability for protection against off-site releases.

Such a program would make sense for a number of important reasons. First and foremost, such mixed waste would become subject to a single set of regulations. Such a result has long been sought by many in the mixed waste field, including DOE, NRC, some members of Congress and virtually all generators and holders of mixed waste. Such a result would not only put a permanent end to inconsistency and duplication of mixed waste regulation, it would also bring badly needed predictability to the mixed waste field, thereby ultimately benefiting the environment as well.

Although the RCRA regulations would need to be amended to make clear that RCRA subtitle C requirements do not apply to mixed waste managed by NRC/DOE, such a proposal has already been suggested by DOE and entertained by EPA in EPA's recent deliberations regarding the definitions of solid and hazardous waste. In the context of that proposed rulemaking (which EPA later withdrew entirely), EPA stated that it "expects that the general approach in today's regulation would allow for exemption of mixed wastes that contain very low concentrations of chemically hazardous constituents . . . there is also a suggestion that for mixed wastes with higher concentrations of chemically hazardous constituents regulated because of RCRA listings, regulation under the AEA already requires measures intended to control exposure to, and releases of, radioactive hazards that would also protect human health and the environment by limiting exposure to, and release of, chemically hazardous constituents from mixed waste. EPA solicits comments as to whether it . . . [should] develop . . . an approach for mixed waste where the conditional exemption criterion would be compliance with regulations that exist to control the radioactivity hazards." (57) Thus, it is possible that EPA would not reject this idea out of hand, since EPA, like others in the mixed waste arena, recognizes the potential benefits to be derived from applying a single set of regulations to some, if not all, mixed waste. In addition, it would also make sense for DOE to revisit its own definition of byproduct material to see if the "direct process" approach, or some similar concept, could be used to eliminate the applicability of RCRA to much of DOE's (and perhaps some commercial) mixed waste streams.



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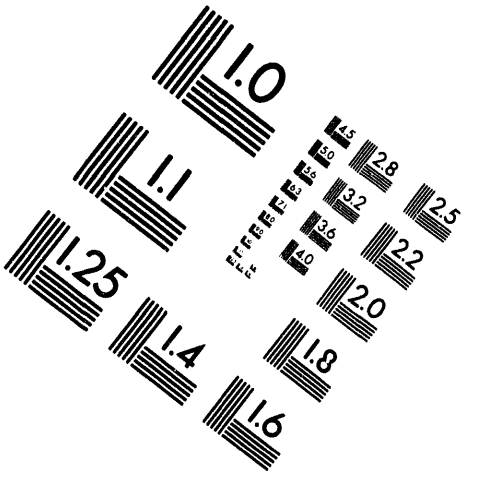

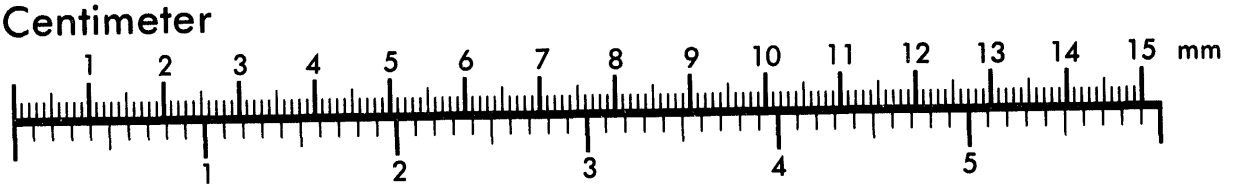

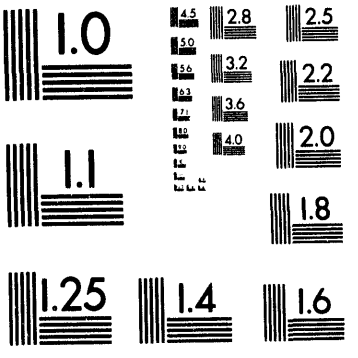

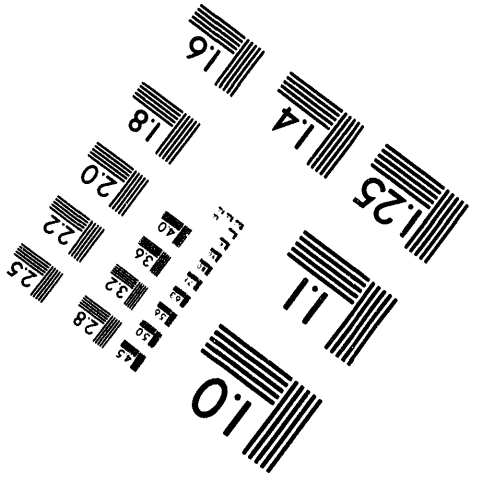

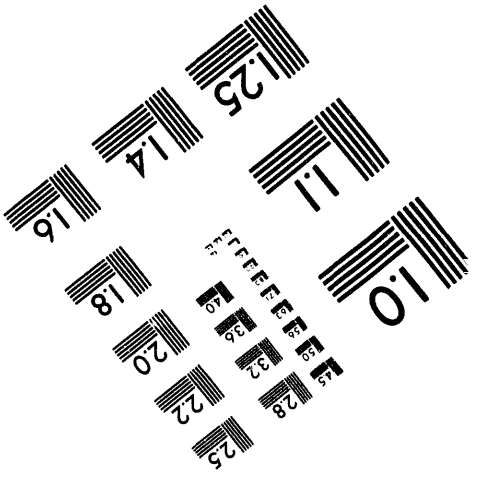

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Given the large volumes of mixed and radioactive wastes already at DOE sites, it makes little sense to move these wastes off-site in violation of NRC's ALARA principal. Thus, DOE wastes would be disposed at on-site DOE disposal units licensed by NRC. Or because some commercial LLRW disposal capacity already exists, some DOE wastes could be disposed of at the existing commercial sites (two of which are located near major DOE facities). For commercial mixed wastes, disposal could take place at either the on-site DOE facilities (for a fee) or at the commercial low-level radioactive waste sites sanctioned or created under the Low-Level Radioactive Waste Policy Amendments Act, (1). Primarily hazardous mixed wastes could be disposed of at RCRA facilities permitted for low-activity wastes.

NRC has already suggested to DOE that it should consider accepting commercial low-level mixed waste at DOE sites. NRC has stated that it does not believe that serious impediments exist to DOE's accepting commercial mixed waste from NRC licensees. (58) On August 2, 1991, the Chairman of NRC wrote the Secretary of Energy to suggest such a plan, which NRC and DOE senior officials are in the process of discussing. (58). The creation of such a plan can easily take place in the context of and consistent with DOE's plan to develop a long-term national compliance strategy for all DOE mixed wastes. (387).

The addition of commercial mixed wastes to either the DOE or commercial sites would not increase the potential overall public health or environmental hazard for the reasons previously discussed. Moreover, the overall volume of such commercial mixed wastes could easily be accommodated at either the existing commercial LLRW sites or at DOE sites. Ultimate ownership by DOE of commercial low-level radioactive waste sites is already required by 10 CFR 61.14 and 61.59, and virtually permanent (i.e., 100 years) DOE ownership of DOE sites is also already assured. Thus, DOE's legal relationships to these wastes would remain essentially unchanged -- except that it would not be forced to contend constantly with on-going RCRA requirements.

The primary benefit of such a system would be that the applicable disposal requirements would acknowledge once and for all that the primary focus of control for mixed wastes that cannot easily be incinerated and that contain significant amounts of radioactivity should be on eliminating the long-term radioactive hazards. Statutory authority could also be provided for NRC to amend its regulations to allow wastes below regulatory concern containing hazardous waste to fall outside the AEA system and be dealt with solely as hazardous waste. Thus, NRC, which possesses the greatest amount of expertise in the radioactive control field, would once again assume the dominant role in the management of such AEA- regulated wastes for these wastes. EPA's concerns regarding the need for enhanced groundwater protection could be met and EPA would maintain a consultative role regarding these wastes consistent with its authority under the 1970 Reorganization Plan No. 3. Presumably, under the NRC/DOE licensing scheme, opportunity for public participation would be legally required as part of the license issuance and Environmental Impact Statement process. However, because of the controversy surrounding such a process, it might also be advisable to create an independent mixed waste oversight and advisory board, similar to the Nuclear Waste Advisory Board, allowing for additional public participation, comment and review. The process of permanently disposing of mixed waste that is not amenable to treatment could begin in earnest. The result would be increased protection of the environment and an overall conservation of scarce government and industry environmental protection resources.

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LSV WASTE DISPOSAL: A SUCCESSFUL COMMERCIAL MIXED WASTE TREATMENT LICENSE AND PERMIT

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ABSTRACT. The U.S. Environmental Protection Agency (EPA) began regulating mixed wastes in the mid-1980's but clear guidance between the U.S. Nuclear Regulatory Commission and EPA was not available for liquid scintillation media at that time. Liquid scintillation media consisted of ^{14}C and ^{3}H in a toluene/xylene liquid mixture which was earlier ruled a mixed waste due to its Resource Conservation and Recovery Act toxicity. The Company wished to engage in the recycle or disposal of the media with licenses and permits by the State of Florida. There was considerable confusion in the regulatory process leading to a permit for a Treatment, Storage and Disposal (TSD) facility in Florida. The Company's application for permit was granted in July 1988 and has been renewed through 1995. From a radiological standpoint, the public safety had to be demonstrated via quarterly monitoring of the cement kiln used for incineration of the low activity media and the Southeast Compact had to allow the unencumbered import of the media to Florida for disposal purposes. In 1985, 70 percent of the media was disposed of in Florida, in 1990 a maximum was reached in media processing. The TSD service for the media disposal continues uninterrupted because of careful handling by the facility and the cooperation of the regulations, generators and brokers of this material. The TSD facility has made an important contribution to the national scene for disposal of the media as mixed wastes and demonstrates the level of cooperation needed to achieve such a result.

INTRODUCTION

Liquid scintillation media (LSV = Liquid Scintillation Vial) processing developed out of a continued need for treatment and disposal and a changed regulatory environment. The EPA began regulating mixed wastes in the mid-1980s; however, due to the lack of definition and jurisdictional disputes between the U.S. Environmental Protection Agency (EPA) and the U.S. Nuclear Regulatory Commission (NRC), clear guidance on how to handle this type of material was not obtainable. When a prohibition of shallow-land burial for mixed waste occurred (in 1985), the processing and incineration option became very important. Regulators on the federal, state and local level helped mold the permit requirements for the Gainesville facility, the first such commercially permitted mixed waste facility. Operations and production changes were needed to adjust to the new regulations. The generators of LSVs and brokers/transporters had to adjust to tighter controls and shipping requirements. The uninterrupted service of the current process depended upon keeping the facility free from major violations and the cooperation of both the regulators and industry users.

Liquid scintillation waste is contained in small glass or plastic vessels (vials) containing 20-30 mL of toluene/xylene as a media for addition and measurement of radioactive materials in trace quantities. This makes the media a mixed waste.

LSVs are in use today for a number of industry applications and medical research. As an example of the medical research application, laboratories apply drug tests on biological tissue with radioactive tracers to

to follow the absorption of an experimental drug. The concept is to administer the drug with a tracer (usually containing ^{14}C or ^{3}H) which can be subsequently extracted and measured at the point of interest. The sample is mixed with scintillation fluid in an LSV to perform a scintillation counting. This measurement determines the efficacy and propagation of the drug for test purposes.

Prior to the use of radioactive tracers, chemical methods required higher dosage for measurement and in many instances, the chemicals as tracers were known to skew chemical balances and invalidate test results. Overall, liquid scintillation counting still remains popular among researchers and although other liquid media may come along, the latter continues to be the mainstay of most research.

The concept of LSV processing had its origin in equipment manufacturing. At the time, the Company intended a business unit to recycle the fluids and vials. There was little interest expressed however, and the Company refocused on the disposal issue.

The problem of disposal continued to worsen and the researchers began to feel more strongly about the meaning of "generator" of radioactive waste (1). The solution appeared to be incineration but it would be important for the existing channels toward disposal (namely the brokers) to provide a complete service (total disposal) to satisfy the generators of such wastes. The Company was impacted by changes in a similar fashion to the rest of the industry - nationally.

REGULATORY HISTORY

There were several regulatory agencies that impacted how mixed wastes such as LSVs were to be handled, changes that would affect procedures all the way from the generators and brokers to the existing process facilities. The most significant was the EPA and its 1984 Hazardous and Solid Waste Amendment (HSWA) (2) which first began to regulate mixed wastes. In January 1986 the "Spent Solvent" rule announced regulation of materials containing greater than 10% toluene/xylene wastes designated for beneficial reuse, and in March 1986 the "Fuel Marketer" rule which required compliance with 40 CFR 266 (3) if bulk hazardous waste fuel was to be burned in energy recovery furnaces. In May 1986, the State did not accept the application as a "Fuel Marketer" by pointing out that the owners of the furnace (in this case, a Solite operated cement kiln owned by the Oldover Corporation) were in fact the "Fuel Marketers." On November 6, 1986, however, the State of Florida DER reversed itself and allowed that Quadrex was the "Fuel Marketer."

The State's reversal was based upon review of EPA's announcement (4), which stated that mixtures of hazardous wastes and radioactive wastes are subject to Resource Conservation and Recovery Act (RCRA) regulation. With this consensus finding, the State of Florida then began to regulate mixed wastes under state hazardous waste rules.

Permit Process

Initially, the Company felt it was exempt from permitting requirements; having a radioactive materials license in place. Counsel for the State DER gave reasons the Company should not be exempt and provided clarification on other points as follows:

1) The Florida statutes regulating radioactive materials under the Atomic Energy Act (5) are not subject to solid or hazardous waste regulation. Further, examples of radioactive materials are uranium, thorium and plutonium. Since the Company was receiving ^{14}C and ^{3}H, the LSVs would not be exempted due to their radioactivity. This conclusion was thought contradictory in that they should have been exempted by virtue of their radioactivity;

2) The LSV were deemed containers by definition (3) of the regulations (40 CFR 261); and to simply empty them would not constitute a treatment process; and finally,

3) The liquid media from the vials was (3) regulated F-Waste or D-Waste (F003, F005 or D001) for blending as a hazardous waste fuel. This latter condition, concluding the Company as a "Fuel Marketer" by blending the media for disposal as a fuel, appeared to be the most important. Counsel for the State DER recommended the DER enter into a Consent Order with the Company to require application for a temporary operating permit (6).

Permitting a Treatment Storage and Disposal (TSD) Facility

The Florida DER exercised its authority to regulate as a "Hazardous Waste Authorized State" (7) in ordering the Company to submit a permit application as a TSD. There is a period of time when companies express denial in opposing regulations such as these but upon evaluating alternatives and measuring the trend for regulation of RCRA wastes, in general, it became clear the permit would be needed and ;the Company proceeded diligently to make application. It was not without difficulty however, when one viewed the chain of involvement from generators to brokers to the TSD and the various states with different degrees of regulation involved in the shipment process. The generators and brokers were required to change existing practices and tighten controls on shipping and transportation of the LSVs even though these wastes were unregulated in most states.

The Company successfully argued that it could continue operations without interruption upon agreement to submit an application for temporary operating permit in April 1987. Application was completed in July 1987 with the Florida DER. The facility was inspected the same month and found totally in compliance. In July 1988 the temporary operating permit was granted (for a two-year period). In January 1990 a Part B application was submitted and subsequently granted in September 1990.

NRC/EPA Regulation of Mixed Wastes

While the Company was struggling with the permit issue in Florida, there were national issues of some substance. In fact, a local Tennessee newspaper (8) published an article stating that a "House Committee (of Congress) admonishes EPA/NRC over dispute." The Congress was referring to a continuing struggle between the two agencies for control of mixed waste regulation, and the definition of mixed waste per se, would not be improved upon.

Items of dispute were:

> Liquid Scintillation Fluids at <0.05 μCi/g of ^{14}C and ^{3}H were considered mixed wastes. If so ruled, every user of LSVs would have to apply for a permit for storage of mixed waste with little regulatory guidance or oversight available on the matter.

The guidance that was available consisted of the joint NRC/EPA Guidance on the Definition and Identification of Commercial Mixed Low Level Radioactive and Hazardous Waste, January 8,1987 (9).

Also, this guidance (9) further confused the process by saying:

> "mixture of toluene and tritium (^{3}H) satisfy the definition of mixed LLW (low-level waste) (9) because they contain listed hazardous wastes (spent toluene and tritium)".

The apparent conflict of this guidance at the generator's level, was that some generators were shipping LSVs initially as hazardous waste only (without regard to the specific activity of ^{14}C and ^{3}H).

Concerns of local bodies and local officials needed to be addressed in addition to state and federal agencies.

In September 1987 the Company wrote both the EPA and the NRC regarding their definition toward regulation of LSVs as mixed wastes where chemical waste brokers were handling and disposing of these wastes without proper license or authority. The response was vague and non-committal, and no resolution was offered (10).

To help resolve the mixed waste issue and to provide the generators and brokers with guidance, the Company agreed to host a joint meeting in Gainesville, Florida, with EPA, NRC, DER, State Radiological Health personnel and local environmental regulators. No consensus could be achieved. As it stood, the requirements on generators were to: 1) obtain generator ID numbers from the EPA; 2) use hazardous waste manifests; 3) require transportation by an authorized hazardous waste hauler; and 4) set a time limit on transportation to the TSD.

RADIOLOGICAL HISTORY

The regulatory scene surrounding the Radiological License was quite interesting. Justification was made in 1983 that the burning of radionuclides did not show an increased risk to public health and safety at the kiln. The request was approved provided quarterly monitoring was performed around the kiln to assure no buildup of radioactive materials in the soil, water, vegetation or the aggregate material. Radionuclides were added to the license (11) in increments; however, this expansion ceased for the following reason: The state law required radioactive waste management firms to conduct a hearing for any major licensing activity. The State essentially stated that adding radionuclides was considered a major activity.

Of additional interest was how bonding requirements were resolved. Since the State DER permit required pollution liability insurance and financial assurance for decommissioning, the State of Florida Radiological Health section also required a bond for decommissioning the LSVs. The company's argument was: There is one governor and a double jeopardy condition existed. The radiological health office issued the license and subsequent renewal without the bonding requirement. The license renewal application was submitted in 1985 and issued in 1990 for five more years (1995). The next renewal application will be made in 1994.

The Southeast Compact has stated in 1986, and have not changed their position to this point, that they will allow for the non-encumbered import of LSVs for the purpose of disposal.

The burning of the fluids has been predominantly with one contract kiln through a radioactive materials license issued by the State to the Company. As expected, the license negotiation process was very detailed and lengthy. Risk benefit analysis and use of existing "de-minimus" decisions were instrumental in the decision-making process. Recently, an amendment was issued to allow for deregulated fluids to be shipped to any authorized hazardous waste burner as long as other state and local regulations are met. The states of Maryland, Illinois and Kansas have balked at allowing deregulated fluids to be burned in their state.

OPERATIONS HISTORY

The LSV process is a complete separation process of the vials (containers) from their content, the liquid scintillation fluid. The process essentially separates the vials from the packing materials, shreds the vials, separates the fluids from the shredded materials and then rinses the crushed vials through a series of dip tanks. The fluids and rinsate are sampled by processor for each generator to assure acceptability. Specific activity of the radiological liquid contents are tested on a liquid scintillation counter for beta emitters and an multichannel analysis for gamma emitters.

There has been a continuing evolution of engineering design and analysis in developing the process. The most significant changes have occurred in the cleaning of the shredded glass and plastic vials. The crusher is the original design from 1983, redesigned to handle more mini-vials since they have become more popular.

The evolution of the cleaning of the crushed glass/plastic vials began with a state-of-the art dryer system. This particular dryer was ineffective due to the resilience of toluene and the hot air taking a path of least resistance. Later, kerosene was used to strip the toluene but left is own film and an odor. Eventually, a proprietary alcohol was used and continues to be used today. Following cleaning, rinsing and drying, the by-product materials (crushed glass/plastic vials) are shipped to an industrial landfill.

Prior to release to landfill, the crushed glass/plastic material is radiologically tested. This testing is based on a model and analysis of the waste rinsate. Testing the rinsates provide for a direct relationship to the surface contamination of the solid materials.

To monitor the by-product solid materials for gamma emitters alone, a 12" G-M tube inside a PVC pipe was developed. This monitor is affectionately called the Company "Proctoscope."

PRODUCTION HISTORY

Table 1 shows USEcology's breakdown of how LSVs were being disposed (by m^3) in 1985 concluding that approximately 70% of the LSV waste nationally was sent to the TSD in Gainesville, Florida. Table 2 shows the volumes of processed drums of LSV since its inception.

Table 1. Processed LSV in (in m^3).

	Exempt	Mixed	Regulated	Total	
TSD Processor	1226	158	368	1,752	(70%)
Burial	0		182	182	(7%)
Other	399	0	171	569	(23%)
Total	1,625		878	2,503	

Table 2. Annual drums processed and the required human resources.

	Year								
Production	1984	1985	1986	1987	1988	1989	1990	1991	1992
Drums Processed	1742	8815	14369	13942	13059	13472	13907	12522	12705
Manhours/ drum	(records not kept)			2.49	2.36	2.14	2.03	2.58	2.45

As can be seen from table 2, the number of drums has reached a maximum as of 1990 and is beginning a decline for the following reasons: 1) The funds available for the disposal of research related waste are decreasing due to reductions in research; and 2) The use of "biodegradable" materials has replaced the xylene/toluene media vials by some investigators. This downward trend may or may not continue.

Table 3 shows that the percent of water has not increased greatly due to the influx of "biodegradable" or "aqueous" based fluids which are being shipped for burning similar to earlier LSVs. This indicates that either the "aqueous" based fluids are not a major factor or this media also has high combustible properties and has not affected overall BTU value (13).

Table 3. Annual value of liquid scintillation media, including hazardous waste fuels blended with liquid scintillation media.

	1987	1988	1989	1990	1991	1992	1993
kCAL. (gram)	21.2	23.2	243.7	23.4	23.2	25.2	23.4
$\%H_20$	26.3	18.5	12.8	16.5	17.8	16.0	14.4
Liters	441,100	509,007	1,047,200	1,572,649	1,410,359	371,127	21,344
%Cl	.2	.55	1.0	1.6	1.5	.6	.5

The continued percent of H_20 in this chart is indication of an environmental consciousness among the laboratories to dispose of this media via the TSD/incineration process rather than down the drain.

CONCLUSIONS

The most responsible position the Company could take was to issue its clients (generators/brokers) a continued disposal option for LSVs. This is because most hospitals and research facilities utilizing LSVs do not have extensive storage capacity and disposal is their chief concern. In pursuing licensing and permitting of the Gainesville facility, the incineration and disposal option was preserved. The Gainesville facility now has 10 years of uninterrupted service without major violations, but it could not have done it alone. The Southeast Compact, as an example, had to adopt export/import policies that would allow LSVs to come to the Gainesville TSD. It is, we believe, through the cooperation of the various regulatory agencies, the Compacts, the brokers and users of LSVs that we have achieved this solution to a mixed waste problem. The Company, for its part, has made a contribution to the national scene for disposal of LSVs, a mixed waste. How other mixed wastes will be treated in the future depends again upon a measure of cooperation of the participants in this industry.

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CHAPTER 4

Vitrification Technologies

COMPOSITIONAL OPTIMIZATION OF MIXED WASTE GLASSES: A MICROSTRUCTURAL APPROACH

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ABSTRACT. Vitrification, an accepted technology for treating high-level nuclear waste, is now being investigated for its potential to process the thousands of tons of low-level and mixed wastes existing in the United States. Generally, a single type of nuclear waste does not possess the necessary balance of components to form a good glass. By utilizing multiple wastestreams and technologies in an integrated approach, vitrification can be effected using only a minimum of additives resulting in volume reduction, more durable endproduct, and reduced costs over competing methods. This is referred to as Minimum Additive Waste Stabilization (MAWS). In this paper we report the results of our research to optimize compositions for vitrification of low level nuclear wastes from Fernald, Ohio using the MAWS approach. About fifty glasses of different compositions have been melted using different percentages of wastes and additives. These glasses were then heat treated at various temperatures. Heat treated and as-melted glass samples were examined using Scanning Electron Microscopy and Energy Dispersive Spectrometry. Various crystalline phases were found, among them fluorophlogopite, forsterite, diopsidic augite and spinels. The composition dependence of crystallization has been studied and near optimal composition has been found for Fernald waste. We have also applied principles of solution chemistry to predict the crystallization behavior as a function of compositional variation, and have shown the usefulness of this procedure in facilitating the determination of optimal composition.

INTRODUCTION

The problem of treating low level mixed nuclear wastes for ultimate disposal has recently come under scrutiny. The levels of radioactivity and other hazardous components are low, suggesting at first glance that the application of the relatively simple technology of cementing could suffice to solve the problem. However, the tremendous volume of waste to be treated and the presence of elements listed as hazardous under the Resource Conservation and Recovery Act (RCRA) leads to additional storage costs and restrictions on ultimate disposal facilities. Thus, vitrification treatment, which has been primarily regarded as a means for disposal of high-level waste, is now being reconsidered for mixed and low-level nuclear waste disposal due to its ability to reduce volume and produce a very durable wasteform. Volume reduction translates directly into savings in storage costs, and there is a further potential for savings if the demonstrated durability of the end product can be made high enough to support a RCRA delisting.

The process of vitrification takes on an added dimension of attractiveness and practicality when applied to situations involving the incorporation of multiple waste streams.

Such a situation exists at the Fernald Environmental Management Project (FEMP) located in Southwestern Ohio at the site of what was, until 1989, a uranium producing operation for the Department of Energy. The FEMP program is now dedicated to the permanent remediation of the problem of accumulated waste materials whose volume and variety present a formidable challenge to safe and cost-effective disposal. The main constituents of the wastepool are about 350,000 m^3 of sludge pit waste, 540,000 m^3 of contaminated

soil under the pits, and about 2.3 mil gal of contaminated waste water. There are also substantial quantities of fly ash accumulated during the operation of the facility's power plant and a diversity of other materials associated with assorted manufacturing and machining operations.

The recognition that vitrification has the potential to combine most, if not all, of these components into a unified waste treatment system has led to the planning and development of the Minimum Additive Waste Stabilization (MAWS) technology. The MAWS concept combines three individual technologies, vitrification, soil washing, and ion exchange waste water treatment which are normally employed separately for site remediation. The integration of these technologies is done in such a way that the various waste streams all become resources for the vitrification process which then requires only a minimum of additives, and the only endproducts are clean soil and water, and a durable glass wasteform for ultimate disposal. This innovative synergistic approach yields greater volume reductions, a more durable endproduct, and substantial cost savings over competing methods (e.g. cementing).

MAWS PROGRAM OVERVIEW

The primary resources for the vitrification process to be applied to the wastes at the FEMP site are the sludges, contaminated soils and, to a lesser degree, the fly ash. These contain both fluxes and glass formers necessary for the glass making process. However, soils contaminated primarily with uranium can be washed with the Lockheed TRUclean process to separate them into clean soils and soil concentrates thereby reducing the volume of soils which must be fed to the melter.

Contaminated waters from the FEMP site and the soil washing will be treated using an ion exchange resin to remove and concentrate the uranium to produce clean water for discharge. The collected uranium will be stripped from the resin and used as feed for the melter.

The melter itself will have an advanced off-gas system with a two stage scrubber designed to produce no secondary waste stream.

More detail on the MAWS program can be found in the paper by I. L. Pegg (1).

WASTE CHARACTERIZATION

Our research program at Catholic University has accumulated an extensive database on glass development for nuclear waste disposal (2,3,4). However, the Fernald waste possesses some unique characteristics which require new approaches other than those used in the past. Dried pit 5 sludge contains as much as 40% magnesium fluoride, a byproduct resulting from the production of uranium metal by reducing UF_6 with magnesium metal. The soil contains large amounts of calcium and additional magnesium owing to the presence of dolmitic limestone. The fly ash to be incorporated into the feed contains significant amounts of organics, which may be the result of oil added to suppress airborne particulates during handling. Table 1 lists the major components in the sludge from one of the pits at the FEMP site, a typical soil analysis as well as an analysis of washed soil/concentrates received from Lockheed after the soil washing operation, and two types of fly ash. These are representative of the major components being dealt with, but do not give an exhaustive picture of the waste at the FEMP site or the range of variation in its components. All analyses in the table were done after heating the samples to 1150°C and holding them at that temperature for 4 hrs. Thus the table does not reflect the organic carbon content in the soils or the fly ash. The unwashed soil from the site typically contains about 5 wt% total carbon of which about 2 wt% is organic. Fly ashes 4A and 5A contain 18 and 56 wt% total carbon respectively. The washed soil concentrate is a blend consisting of 75 wt% inorganic fraction and 25 wt% organic fraction yielding 10 wt% total carbon.

Magnesium and calcium are conducive to the formation of many crystalline phases in silicate melts. Fluorine acts as a flux in glass melts which is useful, but it also enters into some crystalline phases and is another parameter to consider in controlling the viscosity of a melt. The volatility of SiF_4, HF and possibly other fluorides complicates the offgas system design demonstrating, together with the factors mentioned above, the necessity of establishing acceptable limits of fluoride in the feed.

Table 1: Analyzed Composition of Fernald Wastes

	Pit 5 Sludge	Soil	Washed Soil	Fly Ash 4A	Fly Ash 5A
Al_2O_3	2	7.6	8.2	33.2	25.6
B_2O_3	0	0	0	0.2	0.13
BaO	1.9	0	0.1	0.1	0.3
CaO	37	22.1	14.7	1.1	3.6
Fe_2O_3	3.1	3.4	3.6	4.7	13.5
K_2O	0.3	2	2.0	2.5	0
MgO	0	5.3	4.0	0.8	1.8
MgF_2	40	0	0	0	0
Na_2O	0.9	1.0	1.1	0.5	0.6
SiO_2	13.8	56.7	65.1	55.1	52.7
TiO_2	0	0	0.5	1.6	1.3
Other	1.0	1.9	0.6	0.2	0.47

COMPOSITIONAL OPTIMIZATION - BACKGROUND

There are many objectives to be realized in the development of an acceptable glass formulation and in its optimization. The more important ones are:

1. Minimize additive quantity to maximize waste loading.
2. Minimize additive cost.
3. Achieve processability at about 1150°C by maintaining acceptable viscosity, conductivity and low liquidus temperature.
4. Develop ability of glass to withstand the reducing effect caused by organics in the feed.
5. Accommodate a reasonable amount of fluoride in the glass while maintaining processability and waste loading.
6. Allow for variation in wastestream makeup.
7. Maximize durability.

Clearly, the achievement of these objectives involves the formulation, melting, and examination of many different glass compositions. About 50 different compositions have been melted and tested at this time as part of our research program. In this paper we will concentrate mostly on the insights we have gained by studying the microstructures of these formulations as they were produced and after heat treatment to induce crystallization or amorphous phase separation.

EXPERIMENTAL PROCEDURE

The glasses discussed in this study were melted at 1150°C in small crucible batches of about 400 g each. Before vitrification, the Pit 5 sludge was dried at 450°C for 5 hrs, the unwashed soil was dried at 450°C for 4 hrs, and the washed soil and fly ash were dried at 1150°C for 4 hrs. Various proportions of sludge and soil and/or fly ash together with selected additives were vitrified at 1150°C for 1 hr, with stirring for the last 0.5 hour. All of the glasses were melted in Pt/Au crucibles except F5-5 (in clay) and F5-35, F5-36, and F5-37 (in inconel). Some compositions were judged unsuitable on the basis of their behavior during initial melting and subsequent cooling, but others were selected for heat treatment and further study.

Heat treatment was done on 2-3 g samples in covered 5 ml platinum-gold crucibles. A premelt at a temperature above the liquidus was incorporated into the heat-treatment schedule to remove any nuclei or embryos which might have formed upon intermediate cooling and to restore the glass to melter condition. The microstructure of both heat-treated and as melted glass samples was examined in a Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy and Wavelength Dispersive Spectroscopy. Crystal phases were identified on the basis of their morphology, compositions and X-ray Diffraction (XRD) patterns. The quantity of each phase present was determined from SEM images using the image analysis capabilities of our Tracor-Northern (Noran) 5500 system.

In addition to microstructural characterization, viscosity and conductivity were measured.

As the melting program progressed the microstructures and viscosities of the earlier glasses were analyzed and the results used to formulate and melt new glass compositions to expand options for processing and to increase waste loading.

Both the U.S. Environmental Protection Agency Toxic Characteristic Leaching Procedure (EPA TCLP) test and the Product Consistency Test (PCT) (5,6) were used to test the stability of the glasses under aqueous leaching conditions.

RESULTS

Waste Loading and Glass Composition Range

The Fernald glasses melted so far all fall within the composition range represented in Fig. 1. The actual makeup of the glasses, except for the additives, is mapped in Fig. 2. The values plotted in Fig. 2 represent weight percentages of Pit 5 sludge, soil and fly ash on a dried basis. Since the Pit 5 sludge has lost 70% of its weight by drying at 450°C for 5 hrs, the amount of Pit 5 sludge on a wet-basis is much greater. The remaining weight percentage for each point is made up by additives. A single point in Fig. 2 occasionally represents more than one glass melt because of different additive makeup. It is useful to group some of these glasses together in sets to clarify the philosophy that was followed in formulating the melts.

The first set (Set I) of glasses melted included F5-5, F5-7, F5-8, F5-9, F5-10, and F5-11. This set was melted with approximately equal percentages of soil and sludge as a somewhat arbitrary starting point. The effect of various ratios of Na_2O, SiO_2, and B_2O_3 additives on microstructure was studied in this set.

The second set (Set II) of glasses is comprised of F5-12, F5-13, F5-14, F5-15, F5-16, F5-17, F5-18, F5-F5-19, F5-28, F5-29, F5-30. In this set of melts the fraction of sludge was increased. In order to maintain a moderately narrow range of silicon, fourteen to seventeen percent of silica was added to the melts. The effect of varying Na_2O and B_2O_3 with various additions of Al_2O_3, K_2O and Fe_2O_3 was examined. The effectiveness of the soil washing process will impact on the ratio of sludge to soil desired for vitrification. The viscosities of the glasses at 1150°C in this set are all around 2 poise, which is towards the lower limit

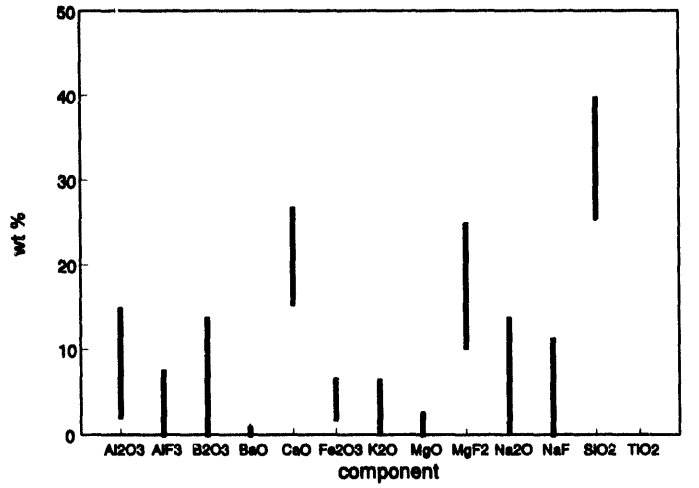

Figure 1 Composition Range of Fernald Waste Glasses

but within the demonstrated acceptable range of viscosity for processing in the GTS Duratek Duramelter vitrification system that will be used for testing and on-site demonstration. According to microstructural observations, F5-12 is about the best composition in this series. In leaching trials it passes the TCLP test and shows good performance on the Product Consistency Test (PCT) at 7 days.

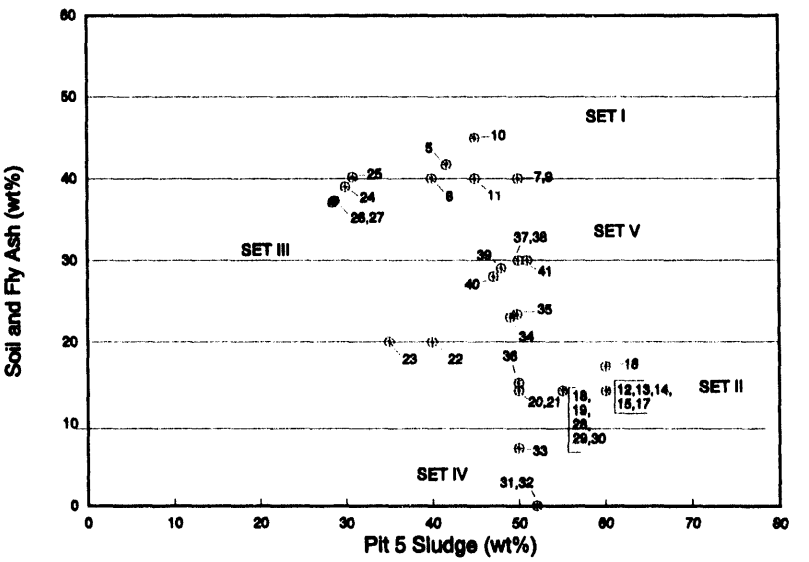

Figure 2 Melting Map (Sludge/Soil and Fly Ash)

The third set (Set III) of glasses (F5-22, F5-23, F5-24, F5-25, F5-26, F5-27) was melted by reducing the waste loading and increasing the level of silicon to increase the viscosity. The viscosities of glasses in this set at 1150°C are around 10 poise. Microstructural observations showed that the glasses crystallize severely under 20 hours 1050°C heat treatment although acceptable behavior at 1080°C was found in one glass (F5-24).

The fourth set (Set IV) of glasses (F5-31, 32, 33) was melted with about 50 wt% sludge, 0-10 wt% soil and about 20 wt% of added silica. The viscosity of F5-33 is 3.3 poise at 1150°C and microstructural observation showed no crystallization under 20 hour 1150°C heat treatment, so F5-33 is considered the best

composition in this set. It also passes the TCLP test. Comparing F5-12 and F5-33, F5-12 has higher waste loading (60 wt% sludge, 14 wt% soil) than F5-33 (50 wt% sludge, 7 wt% soil), and F5-33 has higher viscosity (3.3 poise at 1150°C) than F5-12 (1.4 poise at 1150°C). Silica is relatively easily converted into increased soil loading, especially using washed soil.

The fifth set (Set V) of glasses (F5-34, 35, 37, 38, 39, 40) was melted to test formulations which incorporate fly ash into the feed. Because of the high level of organic carbon in the ash, additional iron was added to the mix to provide a redox cushion to prevent reduction to metal during the initial carbon burnoff.

A sixth set (Set VI) of glasses is being melted which incorporates soil-wash concentrates, but these are not represented in Figure 2 because it is not yet complete. The aim will be to direct compositions into the ranges which have already shown acceptable behavior.

Microstructure

A synopsis of the microstructural results will be given here. A more complete assessment and discussion is being published separately (7). The crystalline phases observed in Fernald glasses are listed along with their formulas in Table 2. There are four fluoride bearing phases: fluorite, fluorophlogopite, pargasite and another fluorosilicate which we have not yet positively identified, but which we suspect belongs to the

Table 2. Phases tentatively identified in Fernald Waste Glasses. At least two other pyroxene group silicates have been observed also and an unidentified fluorosilicate. * Confirmed in some samples by XRD.

*Forsterite	$2MgO \cdot SiO_2$
Diopside	$MgO \cdot CaO \cdot 2SiO_2$
*Fluorophlogopite	$K_2(Mg, Fe^{+2})_6[Si_6Al_2O_{20}](OH,F)_4$
*Pargasite	$(Ca, Na)_{2-3}(Mg,Fe^{+2},Fe^{+3},Al)_5(Al,Si)_8O_{22}(OH,F)_2$
*Fluorite	CaF_2
Haüyne (rare)	$(Na,Ca)_{4-8}(Al_6Si_6O_{24})(SO_4,S)_{1-2}$
*Diopsidic Augite	$(Mg, Fe^{+2})(Ca,Fe^{2+})Si_2O_6$
*Aluminian Augite	$Ca(Mg,Fe^{+3},Al)(Si,Al)_2O_6$
Spinel, iron oxides	$Fe^{+2}(Fe^{+3},Cr)_2O_4$, Fe_3O_4, Fe_2O_3

amphibole silicate family as does pargasite. Since the most important objective in the cleanup of the FEMP site is the vitrification of all of the sludge, we will concentrate here on the microstructures observed in Set II, which represents the highest sludge loading of the groups discussed above. Table 3 shows compositions of these glasses from the wastes and additives used. Note that waste loadings on an "as-is" basis are considerably higher for these wastes due to the high content of water, carbonates, hydroxides, etc., which are lost upon vitrification.

The properties of the as-melted glasses are shown in Table 4. Note that F5-12, F5-15, and F5-18 contain no crystals. Amorphous phase separation was observed in F5-14 and F5-16. Dark spherical globules enriched in aluminum and depleted in calcium and magnesium relative to the glass were found dispersed throughout. These were about 0.2 μm in diameter in F5-16 (Figure 3) and about 1 μm in diameter in F5-14.

Table 3. Dry Feed Make Up and Composition of Glasses in Set II

Dry Feed	F5-12	F5-13	F5-14	F5-15	F5-16	F5-17	F5-18
Pit 5	60	60	60	60	60	60	55
Soil	14	14	14	14	17	14	14
SiO_2	14	14	17	14	14	14	14
Na_2O	5	3	0	0	0	0	5
B_2O_3	7	6	6	6	6	3	6
Al_2O_3	0	3	3	6	3	9	6
Composition calculated on basis of dry feed.							
Al_2O_3	2.13	5.71	5.71	9.28	5.97	12.86	9.07
B_2O_3	8.34	7.15	7.15	7.15	7.20	3.58	7.06
BaO	1.06	1.06	1.06	1.06	1.06	1.06	0.96
CaO	23.53	23.53	23.53	23.53	24.34	23.53	21.53
Fe_2O_3	2.20	2.20	2.20	2.20	2.32	2.20	2.03
K_2O	0.42	0.42	0.42	0.42	0.48	0.42	0.40
MgO	0.71	0.71	0.71	0.71	0.87	0.71	0.70
MgF_2	22.23	22.23	22.23	22.23	22.38	22.23	20.11
Na_2O	6.60	4.22	0.65	0.65	0.68	0.65	8.48
SiO_2	31.98	31.98	35.55	31.98	33.85	31.98	30.93
Other	0.79	0.79	0.79	0.79	0.86	0.74	0.74

Table 4. As-melt Properties

F5-12	No crystals
F5-13	Interfacial crystals at Pt-Au crucible surface
F5-14	Phase Separated
F5-15	No Crystals
F5-16	Phase Separated
F5-17	Crystalline - Phlogopite Series - 1 vol%
F5-18	No Crystals - optical microscopy only

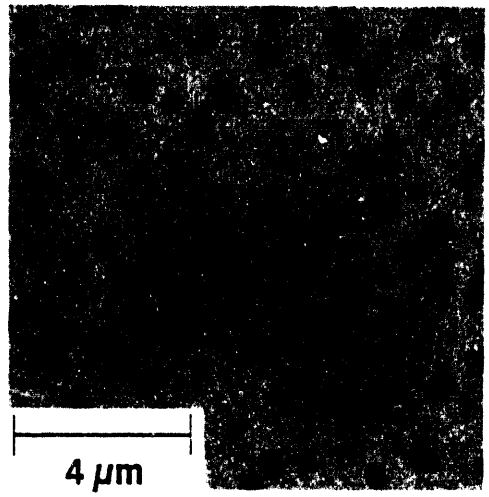

Figure 3. F5-16, as melted, phase separation.

This separation probably occured during cooling from melt temperature. A milky green appearance in some regions of F5-17 suggested that it too might be phase separated, but we did not find evidence of this in our SEM sample. Diopsidic augite was the only major phase to form in F5-14 and F5-16 upon heat treating, and these were the only two glasses of the series in which it did develop. This may be related to their higher silica content. Aluminian augite grew to a level of 40 vol% in F5-17 upon heat treatment which is consistent with its high alumina content. The only two glasses to exhibit crystals in the as-melted state were F5-13 and F5-17. In F5-13, the percentage was much less than 1 vol% and may have been mostly an interfacial effect since crystals were only found near the crucible contact surfaces. The only difference between F5-15 which did not contain crystals as-melted and F5-13 was the substitution of 3 wt% Al_2O_3 by 3 wt% Na_2O in the latter. This would be expected to suppress crystallization and, in fact, F5-13 had the lowest heat treated crystallinity of set II.

Table 5 lists the crystal phases and quantities for 1050°C 20 hour heat treatments in these glasses. We are focusing on this temperature because it is 100°C below the designed melter operating temperature. Ideally one would like to maintain the melter temperature 100°C above the highest liquidus in the glass to provide a safety cushion for composition and temperature deviations, power failures, and any other minor process variations. Although 20 hours is probably extreme, it provides an indication of the probable evolution of the system under stressed conditions.

The behavior of fluorophlogopite crystallization in one of the Fernald glasses (F5-15) has been systematically studied in some detail, and the results are being published separately (8). Fluorophlogopite frequently appears to be the first phase to crystallize in Fernald glasses which makes it a useful tool in a simple analysis of kinetics to be presented later. Fluorophlogopite is often observed to be surrounded with the unidentified fluorosilicate phase referred to in Table 2. Fluorophlogopite contains essentially no calcium while the accompanying phase does, although at a lower mole fraction than the glass. At a later stage of crystal growth pargasite may nucleate and grow at the edge of the fluorosilicate. The mole fraction of calcium is higher in pargasite than in the fluorosilicate, but still less than in the glass. Finally, at a still later stage dendritic fluorite which is higher still in calcium may nucleate at the periphery of the pargasite growth. Figure 4 displays the end result of this process in F5-17 as-melted. The entire growth pattern is indicative of a progressive local enrichment of the melt in calcium by segregation from the advancing phase(s). The compositional progression in the sequence is consistent with and suggestive of

fluorophlogopite being the initial phase to nucleate.

Table 5. The quantity of crystal phases in heat-treated glasses in set II (Heat treatment 1050°C, 20 hour; Premelt 1100°C, 1 hour; Tr=Trace quantities)

	F5-12	F5-13	F5-14	F5-15	F5-16	F5-17	F5-18
Forsterite	5.0	1.0	<1.0	0	0	0	6.0
Diopsidic Augite	0	0	2.0	0	3.0	0	0
Fluorophlogopite	0	<1.0	<1.0	5.5	<1.0	6.0	Tr
Pargasite	0	0	0	13.8	0	Tr	0
Fluorite	0	0	0	0	0	8.0	0
Unidentified Fluorosilicate	0	0	0	3.0	0	7.0	0
Aluminian Augite	0	0	0	0	0	40	0
Total	5.0	<2.0	<4.0	22.3	<4.0	61.0	6.0

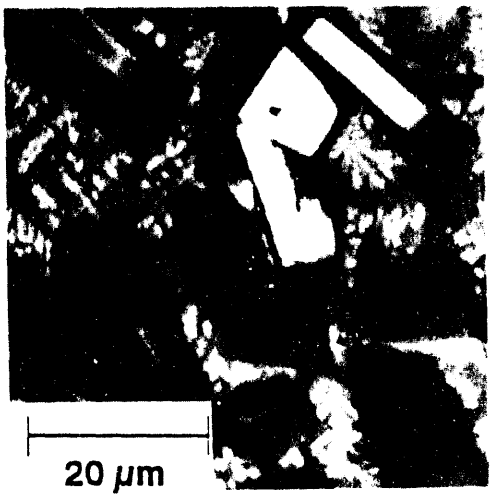

Figure 4. F5-17, as melted. Bright large crystal: fluorophlogopite; Dark crystal: Unidentified Fluorosilicate; Low contrast crystal: Pagasite; Bright dendritic crystal: Fluorite.

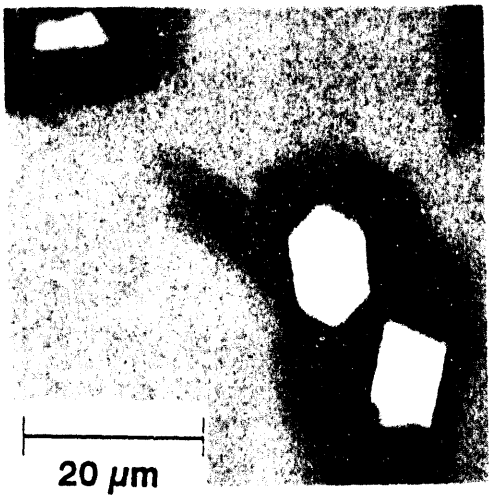

Figure 5. F5-15, 1050°C, 20 hours. 1 hour 1100°C premelt. Bright crystal: Fluorophlogopite Dark crystal: Unidentified fluorosilicate Low contrast crystal: Pargasite.

Not all of the glasses exhibit all four stages of this growth process. Figure 5 shows the microstructure of F5-15 heat treated at 1050°C for 20 hours and in which only the first three phases mentioned above have developed. The only difference between F5-15 and F5-17 is that in the latter 3 wt% of the boron was replaced by aluminum. This caused F5-17 to crystallize massively under heat treatment (~61 vol% crystalline) while F5-15 was about 22% crystalline. Comparing entries in Table 3 and Table 5 it can be seen that there is usually a correlation between elevated aluminum content and increasing crystallinity in this set of glasses. The one exception to this is F5-18 which is only 6 vol% crystalline despite having about the same aluminum content as F5-15. This glass was made by decreasing sludge loading by 5% and

replacing it by Na_2O. This means that Si, Mg, F and Ca come down slightly but the main change is in Na_2O, and it seems to resolve a majority of the crystallization caused by the aluminum.

The only two glasses to contain more than 1 vol% forsterite are F5-12 and F5-18. They are both relatively high in Na_2O and F5-12 contains about 1 vol% more B_2O_3. The fact that F5-18 is about 6% higher in Al_2O_3 does not impact much on the microstructure. Aluminum is a constituent of fluorophlogopite and this accounts for the trace of fluorophlogopite in F5-18, but it could have been much higher had the soda level been lower. Despite the elevated soda level, PCT results are acceptably below the Savannah River Laboratories - Environmental Assessment limits.

The only difference between F5-14 and F5-16 is that 3 wt% soil was exchanged for 3 wt% silica in the latter. The microstructures are extremely similar. The 1 vol% increase in diopsidic augite reflecting the slightly elevated calcium and magnesium levels. This confirms in this composition range the convertability of soil and silica within moderate limits.

From these results we observe changes in sodium level to have a profound effect on crystallization. In particular, it expands the upper limit for acceptable aluminum content. Increasing aluminum is a problem in this composition range because it is a component of several crystal phases which have liquidus temperatures close to 1050°C. Although it is not immediately evident from set II glasses, increased boron also helps to suppress crystallization. One can see it is not easy to make a systematic interpretation of data from multicomponent systems. In the next section we will present an approach based on simple reaction kinetics which aids in structuring this data.

MODELING

To predict liquidus temperatures in a multi-component melt solely on the basis of composition is a challenging problem in theoretical physical chemistry which defies an exact solution even with the best knowledge of the chemical and physical properties of the melt.

A simplified approach to the problem is necessary if one is to determine how liquidus temperature shifts as melt composition is altered. A method with which we have achieved some degree of success is described below.

Following standard treatments (9) the change in molar Gibbs free energy, $\Delta\mu^\circ$, and the molar heat of formation Δh°, of a species during crystallization are dependent on the physical conditions and composition of the melt. If a melt composition range exists for which $\Delta\mu^\circ$ and Δh° remain relatively constant we can apply simple reaction equilibrium to the crystallization process to establish some useful relationships. The equilibrium constant, K_x, can be related to $\Delta\mu^\circ$ as follows:

$$\Delta\mu^\circ = -RT\ln K_x \qquad (1)$$

where T is the liquidus temperature of the species under consideration, and K_x depends only in the initial mole fractions in the melt of the components which constitute the specific crystal phase under consideration. Taking the derivative of both sides of equation (1) with respect to T gives

$$\frac{dT^{-1}}{d(K_x)^{-1}} = \frac{R}{\Delta h^\circ} \qquad (2)$$

The dependence of Δh° on T is normally very small so it will be considered constant over the temperature range of interest. Since Δh° is negative for crystallization, the liquidus temperature T decreases when $(K_x)^{-1}$

decreases. This implies that for a fixed temperature there is a critical value $(K_x)_c^{-1}$ which, when exceeded, will result in crystallization and below which, no crystallization will occur.

We have tested this approach using our data on Fernald nuclear waste glasses, which have been melted at various compositions in the ranges represented in Fig. 1. For fluorophlogopite and diopsidic augite, which are two frequently occurring crystal phases limiting processing, Fig. 6 and Fig. 7 show that there appears to be a critical $(K_x)^{-1}$ value for each crystal phase at 1050°C. These values for K_x were calculated from the calculated compositions of the Fernald glasses. In general, we have found that the calculated and analyzed compositions agree within ± 10%. According to Fig. 6 and Fig. 7, the $(K_x)^{-1}$ values for both fluorophlogopite and diopsidic augite in F5-20 are just above the $(K_x)_c^{-1}$ values respectively. Fluorophlogopite and diopsidic augite might not crystallize from the glass, if F5-20 were heat-treated at a slightly higher temperature (above 1050°C). We tested this hypothesis by heat-treating at 1070°C for 20 hrs after 1 hr 1100°C premelt. Neither fluorophlogopite nor diopsidic augite crystallized from the glass, and only about 1 vol% of forsterite was found in the heat-treated sample. Further experiments are in progress to determine the critical $(K_x)^{-1}$ values at other temperatures. Then it should be possible to use Equation (2) to calculate the critical values for any temperature within a reasonable range. Those critical values can then be used to predict the crystallization behavior of compositions yet to be melted.

The next step will be to experiment with other compositions within the range specified by Fig. 1 to see if the behavior is well sustained there, and then to begin excursions outside of this range to determine the limits of compositional variation within which predictability remains good. In the case of diopsidic augite there is already some evidence that fluoride concentration (which does not enter into K_x for diopsidic augite) above a certain limit may lead to crystallization. Applying only the method outlined above, this would not be expected. Our evidence for the unusual effect of fluorine on diopsidic augite formation is F5-32, where diopsidic augite formed even though the K_x value was below the critical value of -7.2.

While refinements are possible and are being explored, even a simple correlation such as the one described above can greatly reduce the number of experiments necessary if the underlying database for composition is sufficiently broad.

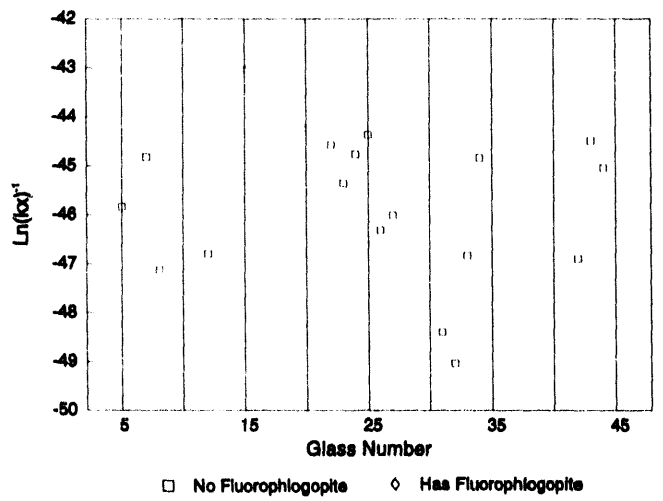

Figure 6. $Ln(Kx)^{-1}$ values for fluorophlogopite

Several other crystalline phases (Table 2) have been observed in Fernald glasses. We have only applied our method to diopsidic augite and fluorophlogopite, and only in cases where it appears fairly clear that these are the first phases to crystallize. The reason for this is that once one phase starts to crystallize the remainder of the melt, especially in the vicinity of the crystals, will be altered in composition, and the value of K_x for other phases will change, perhaps significantly. As described above, we have observed ordered intergrowth of up to 4 phases which is attributable to the segregative depletion or enrichment of some component in the melt around a crystallizing phase.

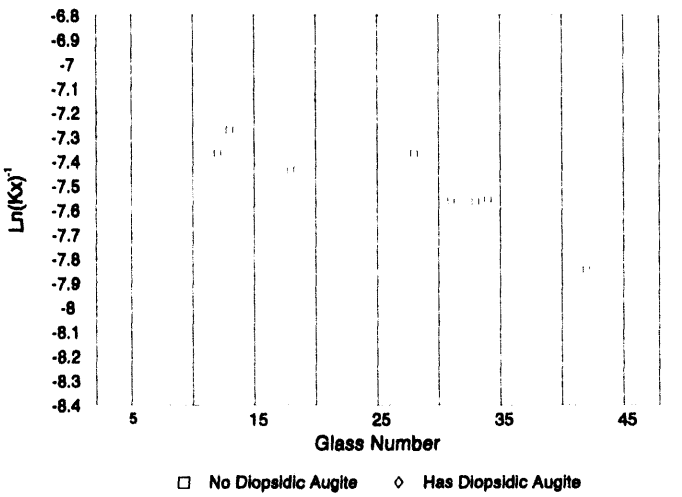

Figure 7. $Ln(kx)^{-1}$ values for diopsidic augite.

CONCLUSIONS

At this point we have demonstrated the ability to make acceptable glass wasteforms, over a broad range of combinations of waste materials from the FEMP site. Crystalline phases likely to occur in these glasses have been identified and their possible impact on wasteform performance has been and continues to be assessed through heat treatment and observation of test glasses. Adjustments of Boron, Sodium and Aluminum levels in trial melts has been especially important in the compilation of a database which will ensure the compounding of processable and durable glass over the range of component waste fractions likely to be incorporated into melts in the process of vitrification. With more work yet to be done, we have successfully begun modeling behavior of the melt using simple chemical reaction kinetics and are in the process of expanding and refining this approach to make it a useful tool for establishing acceptable glass behavior and guiding the choice of new compositions. Using this approach we have determined a critical value of K_x for fluorophlogopite by analyzing 1050°C 20 hr heat treatment data for glasses produced thus far.

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REACTIVE ADDITIVE STABILIZATION PROCESS FOR HAZARDOUS AND MIXED WASTE VITRIFICATION

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ABSTRACT. Solidification of hazardous/mixed wastes into glass is being examined at the Savannah River Site for (1) nickel plating line (F006) sludges and (2) incinerator wastes. Vitrification of these wastes using high surface area additives, the Reactive Additive Stabilization Process (RASP), has been determined to greatly enhance the dissolution and retention of hazardous, mixed, and heavy metal species in glass. RASP lowers melt temperatures (typically 1050-1150°C), thereby minimizing volatility concerns during vitrification. RASP maximizes waste loading (typically 50-75 wt% on a dry oxide basis) by taking advantage of the glass forming potential of the waste. RASP vitrification thereby minimizes waste disposal volume (typically 86-97 vol. %), and maximizes cost savings. Solidification of the F006 plating line sludges containing depleted uranium has been achieved in both soda-lime-silica (SLS) and borosilicate glasses at 1150°C up to waste loadings of 75 wt%. Solidification of incinerator blowdown and mixtures of incinerator blowdown and bottom kiln ash have been achieved in SLS glass at 1150°C up to waste loadings of 50% using RASP. These waste loadings correspond to volume reductions of 86 and 94 volume %, respectively, with large associated savings in storage costs.

INTRODUCTION

Technologies are being developed by the U.S. Department of Energy's (DOE) Nuclear Facility sites to convert low-level and mixed wastes to a solid stabilized waste form for permanent disposal. One of the alternative waste forms is vitrification. The U.S. Environmental Protection Agency (EPA) has declared vitrification the Best Demonstrated Available Technology (BDAT) for high-level radioactive waste (1) and produced a Handbook of Vitrification Technologies for Treatment of Hazardous and Radioactive Waste (2). The DOE Office of Technology Development has taken the position that mixed waste needs to be stabilized to the highest level reasonably possible to ensure that the resulting waste forms will meet both current and future regulatory specifications. Vitrification produces durable waste forms at volume reductions up to 97% (3). Large reductions in volume minimize long-term storage costs making vitrification cost effective on a life cycle basis (4). The U.S. DOE Savannah River Site (SRS), which is operated by Westinghouse Savannah River Company (WSRC), is currently investigating vitrification for disposal of various low-level and mixed wastes (3,5). The first hazardous/mixed wastes vitrified in laboratory studies at SRS have been (1) incinerator and (2) nickel plating line Resource and Recovery Act (RCRA) F006 wastes. Vitrification into simple glass compositions was achieved by tailoring the glass composition to take advantage of the common glass constituents-Si, Al, Na, and Ca-already in the waste. Stabilization of the heavy metals in the glass is achieved by use of reactive additives such as diatomaceous earth, perlite (perflo), rice husk ash, and/or precipitated silica. The process/product models developed for high level radioactive waste glass were utilized to develop glass formulations which optimize glass processability, e.g viscosity, and product durability (6).

Nickel-Plating Line Wastes

The M-Area operations at the Savannah River Site (SRS) in Aiken, South Carolina, produce reactor components for nuclear weapons materials for the DOE. The resulting waste is a mixed F006 waste which is currently being stored in the Process Waste Interim Treatment/Storage Facility (PWIT/SF). The total current volume in storage was initially ~1,200,000 gallons of which ~25% is a gelatinous hydroxide sludge. There is approximately 210,000 gallons of F006 waste sludge which is high in nickel and uranium. It has been demonstrated (7) that a volume reduction of 65-70% of the M-Area waste can be achieved by wastewater treatment of the supernate, with the resulting effluent released via a NPDES outfall. About 450,000 gallons of spent SiO_2 rich filter aids (perlite/perflo) will be generated from the supernate treatment.

In January 1989 South Carolina Department of Health and Environmental Control (SCDHEC) approved a construction permit for the DETF Supernate Transfer Facility. This allowed the DETF to be used to treat the supernate from the M-Area Interim Storage/Treatment Facility tanks. There are six 35,000 gallon tanks (Tanks 1-6) and three 500,000 gallon tanks (Tanks 7, 8, 10). Tanks 1-7 are full. Tank 10 is currently being filled with spent filter aid materials. Treatment of the supernate from Tank 8 was completed in November, 1992. Treatment of the supernate from Tank 7 is in progress. Treatment of the supernate in the remaining tanks will occur sequentially.

The sludge and spent filter aid wastes are to be homogenized into one batch before final stabilization/solidification. Volume reductions on the order of ~50%, were demonstrated by mixing portland cement with the sludge/spent filter aid, followed by pressure filtration and rinsing. This process has been designated FIST for FIltration and STabilization process (7,8).

Incinerator Ash/Incinerator Blowdown Wastes

The Consolidated Incineration Facility (CIF) is a facility under construction for the DOE at the SRS in Aiken, South Carolina (9). The CIF is a rotary kiln incinerator that will thermally destroy toxic constituents and volumetrically reduce both solid and liquid waste materials. Subsequent stabilization is required to allow disposal of the wastes (9,10). The facility will handle a variety of waste types which are categorized within the classifications of low-level-radioactive, hazardous and/or mixed waste. The facilities design criteria require that operation be controlled within the limits of the RCRA permit approved by the SCDHEC (10).

The CIF is designed to allow simultaneous processing of high heat content liquid organic waste; low heat content aqueous solutions, and boxed low-level radioactive/mixed hazardous solid waste in the primary combustion rotary kiln (RK). Combustible wastes fed into the RK are volatilized, and a partially oxidized flue gas is produced. Noncombustible aqueous solutions evaporate (10,11). Flue gases from the rotary kiln enter the secondary combustion chamber (SCC) at a controlled minimum temperature of 1000°C where the kiln exit gases are processed at >1200°C to assure complete combustion and to decompose any unburned organic toxic constituents. Additional high heat content radioactive organic liquid waste is simultaneously injected into the secondary combustion chamber for destruction at >1200°C.

The CIF generates two secondary mixed waste streams that require treatment before disposal (12). The first is the rotary kiln bottom ash, a heavy ash residue produced primarily from the rotary kiln combustion but also containing materials from the SCC. Current plans are to solidify the accumulated ash in drums by mixing it with cement to form a stable mixture referred to as "ashcrete." The second waste stream from the CIF is the off-gas scrubbing liquor (blowdown). These liquids must be treated as radioactive process by-products. This blowdown waste contains chloride salts produced from the neutralization of acid gases and entrained flyash from the kiln. The blowdown contains approximately 80 wt% water and 20 wt% chloride salt, ash, radioactive, and hazardous contaminants that were entrained or volatilized during

incineration. Liquid blowdown will be more difficult to stabilize than bottom ash because of high halide concentration, soluble heavy metals, and radionuclides.

EXPERIMENTAL

The nickel plating line waste glasses were made of actual nickel plating line sludge and spent filter aid (perlite/perflo) by adding reagent grade chemicals. Waste loadings varied from 90 to 70 wt%. The incinerator waste glasses were made from simulated ash and simulated blowdown using reagent grade chemicals and varying sources of SiO_2, e.g. silica sand, diatomaceous earth, Perlite, or pyrolyzed rice husks. Waste loadings were varied from 30 to 50 wt% waste on a dry oxide basis. Initial glass formulations were determined by substitution of Na_2O for NaCl since simulation of dechlorination by pyrohydrolysis (13) is difficult to achieve in crucible studies. Two glasses were made with the reference amounts of NaCl and water in an attempt to pyrohydrolyze the NaCl in a crucible.

All glasses were melted at temperatures between 1150° and 1300°C in high purity Al_2O_3 crucibles for 4 hours. Small amounts of glass, ~100 gram batches, were made to optimize the best compositions for further testing.

Each vitrified sample was submitted for x-ray diffraction (XRD) analysis so that the homogeneity of the resulting glass could be determined. For glasses which were not homogeneous, the crystalline phases were identified by XRD. If analysis by XRD was inconclusive, elemental scans by x-ray fluorescence (XRF) were substituted.

A modified EPA Toxicity Characteristic Leaching Procedure (TCLP) was performed at the Savannah River Technology Center (SRTC) on representative homogeneous glasses and one incompletely reacted CIF simulated waste glass.

RESULTS AND DISCUSSION

Reactive Additive Stabilization Process (RASP)

Reactive high surface area silica, as a waste form additive, was determined to greatly enhance the solubility and retention of hazardous, mixed and heavy metal species in glass. Highly reactive silica was found to increase the solubility and tolerance of Soda(Na_2O)- Lime(CaO)-Silica(SiO_2) glass (SLS) and borosilicate (B_2O_3-SiO_2) glass formulations to atomistically bond the waste species. Highly reactive silica lowers glassification temperatures, increases waste loadings which provides for large waste volume reductions, and produces EPA acceptable glasses. The RASP can be used to vitrify (1) spent filter aids from wastewater treatment, (2) waste sludges, (3) combinations of spent filter aids from wastewater treatment and waste sludges, (4) combinations of supernate and waste sludges, (5) incinerator ash, (6) incinerator off-gas blowdown, (7) combinations of incinerator ash and off-gas blowdown, (8) cement formulations in need of remediation into glass, (9) ion exchange zeolites, (10) inorganic filter media, (11) asbestos or glass fiber filters, and (12) radioactive materials including transuranic wastes.

Nickel-Plating Line Glasses

The M-Area nickel plating line waste sludges plus the spent filter aid from the associated supernate treatment are examples of RASP stabilization. Representative samples of the RCRA F006 sludge in each of the M-area tanks, including the tank with the spent filter aid, was analyzed between 1987 and 1993. X-ray diffraction analysis of the sludges dried at 90°, 300°, and 600°C allowed the chemical phases to be identified and a molar mass balance calculation to be performed (Table 1). The aluminum is present

primarily as $Al(OH)_3$, while the Na is present as $NaNO_3$. Using the current and projected tank volume inventories a calculated composite waste composition based on a dry calcine basis was determined (Table 1).

Table 1. M-Area calculated composite sludge composition.*

Oxide	Wt%	Oxide	Wt%	Mass Balance Speciation	Wt%**
Al_2O_3	17.47	TiO_2	0.04	$Al(OH)_3$	23.18
CaO	0.48	K_2O	1.48	$NaNO_3$	17.88
Fe_2O_3	0.88	P_2O_5	3.22	SiO_2	43.44
MgO	0.20	BaO	0.02	$Na_6U_7O_{24}$	3.48
MnO	0.28	PbO	0.11	Ca-zeolite	3.15
Na_2O	10.83	MoO_3	0.01	$AlPO_4$	4.32
NiO	0.93	ZnO	0.59	SUM	95.44
SiO_2	43.58	CuO	0.03		
Cr_2O_3	0.01	SO_4	0.03		
B_2O_3	0.03	NO_3	13.05		
UO_2	3.00	SUMS	96.28		

*Current inventory plus additional filter aid projected from continued supernate treatment.
**Species identified by x-ray diffraction analysis.

The high SiO_2, Al_2O_3 and Na_2O content of the M-Area waste indicated that stabilization in either sodium borosilicate or SLS glass was feasible. The addition of only one additive, B_2O_3, borax ($Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$), or $Na_2O{\cdot}B_2O_3$ enabled the waste mixture to be made into a borosilicate glass (Fig. 1, Table 2) while the addition of only $CaCO_3$ or a mixture of $CaCO_3$ and Na_2CO_3 allowed solidification into SLS glass (Fig. 2, Table 2). The use of only one additive simplifies processability of the waste as only two components need to be adjusted in order to optimize processability and waste loading (Fig. 1).

Vitrification was achieved in both borosilicate and SLS glass at waste loadings varying between 70 to 90 wt% waste (Table 2). Higher waste loadings were achieved at higher melt temperatures. Homogeneous glasses formed at 1150°C at waste loadings of 70 to 80 wt%. The borosilicate system is a well known glass forming system used to make commercial pyrex and vycor glasses which are very stable but are phase separated. Many types of high-level radioactive wastes are being solidified in borosilicate glasses which are in the known glass forming region of the Na_2O-B_2O_3-SiO_2 system, but away from the known region of phase separation (14). Phase separation is undesirable for waste stabilization because phase separated glasses tend to be less durable than homogeneous glasses (15).

M-area waste glass formulations are being optimized in the region of the borosilicate system-where the high-level radioactive waste glasses are known to form stable homogeneous glasses. The process models developed for high level borosilicate waste glasses can be utilized to calculate the glass viscosity and durability as a function of temperature (6).

Table 2. Glass formulations and additives for M-Area sludge with spent filter aid.

Glass	Waste Wt%*	Melt Temp. (°C)	Type of Additive	Type of Glass	Results
M-1	90	>1300	Borax	Borosilicate	Poorly Melted
M-2	85	>1300	Borax	Borosilicate	Poorly Melted
M-3	90	>1300	H_3BO_3	Borosilicate	Poorly Melted
M-4	90	>1300	$CaCO_3$	SLS	Poorly melted
M-5	80	>1250	H_3BO_3 + Na_2CO_3	Borosilicate	Poorly melted
M-6	70	1150	Borax + Na_2CO_3	Borosilicate	Homogeneous Glass
M-7	80	>1150	$CaCO_3$ + Na_2CO_3	SLS	Poorly melted
M-8	70	1150	Borax	Borosilicate	Homogeneous Glass
M-9	70	1150	$CaCO_3$ + Na_2CO_3	SLS	Homogeneous Glass

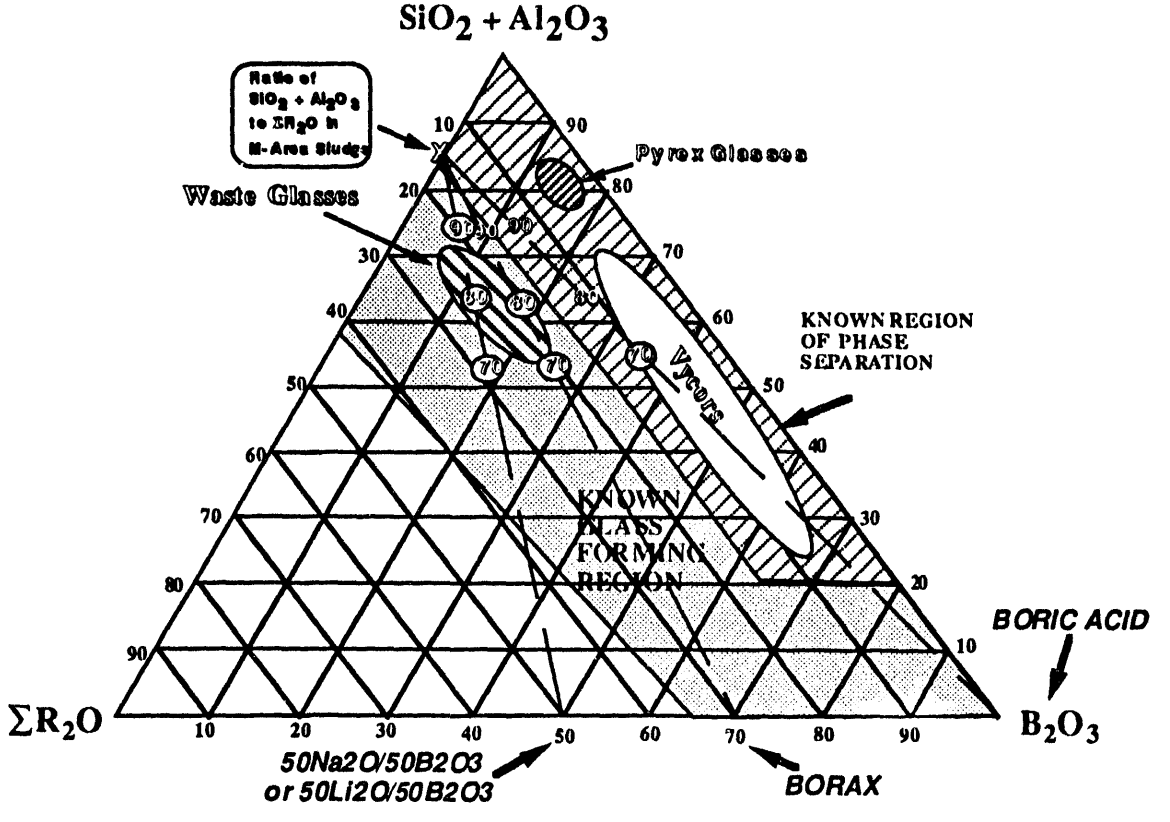

Figure 1. Ternary phase diagram for the system Na_2O-B_2O_3-SiO_2 with the glasses formulated for M-Area sludges superimposed (wt%). The "X" indicates the ratio of SiO_2 + Al_2O_3 to the alkali oxides (R_2O) in the M-Area sludge and filter aid. The stippled area indicates the known glass forming region in the Na_2O-B_2O_3-SiO_2 system. The cross hatched area indicates the known region of phase separation and includes the commercial pyrex and vycor glasses. Glasses in the region of phase separation tend to be less durable than glasses in the other region of the Na_2O-B_2O_3-SiO_2 system.

The SLS glass forming system is a well known system used to make window glass and it has been extensively studied by glass chemists since 1925 (16-19). Soda-silica glass is known to readily incorporate heavy metals (20). SLS glass formulations have been used for In-Situ Vitrification to solidify contaminated soils (21-22) and a barium analog (soda-baria-silica) glass has been used at Fernald to solidify residues from uranium ore processing that contain large amounts of uranium, radium, and lead (23). For Fernald waste solidification the barium rich glass was chosen due to the high barium content of the waste. SLS glasses have also been successfully fabricated from reactive sodium metal contaminated during efforts to develop sodium-cooled fast breeder nuclear reactors (24). For the M-Area wastes, Fig. 2 demonstrates that the use of reactive silica, in this case the spent filter aid already a part of the waste, extends the known glass forming region in the SLS system.

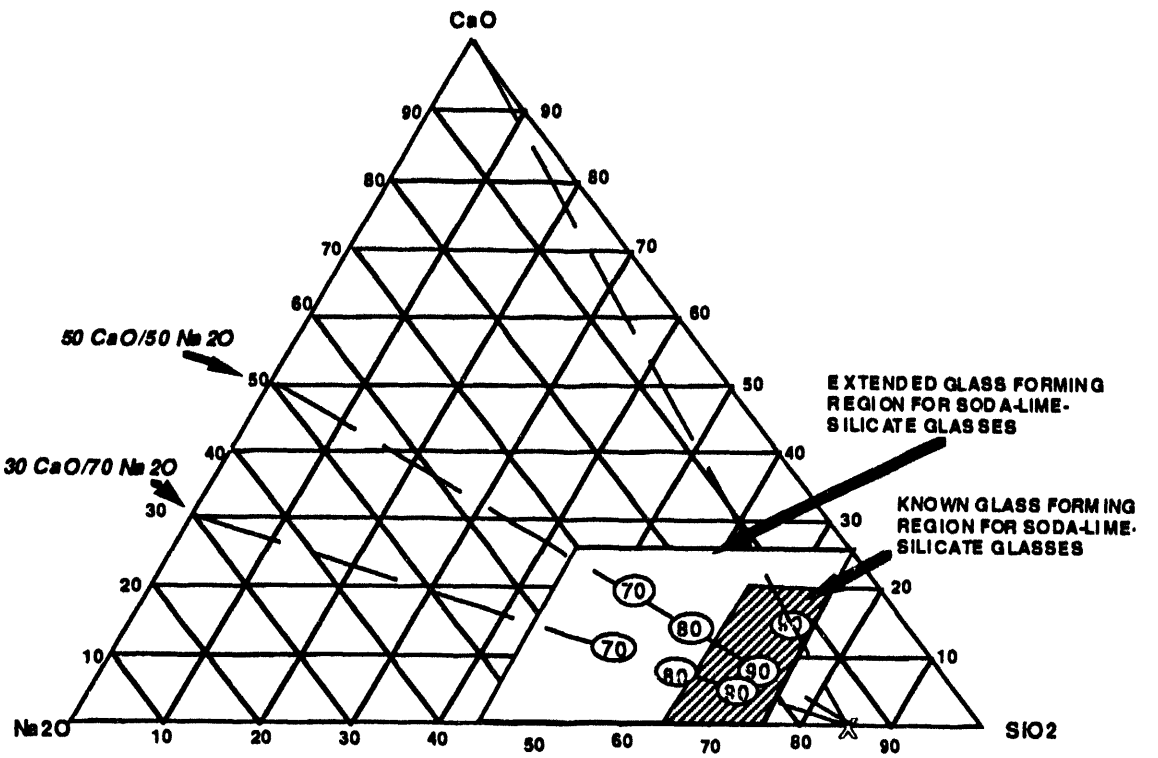

Figure 2. Ternary phase diagram for the system Na_2O-CaO-SiO_2 with the glasses formulated for M-Area sludge superimposed (wt%). The "X" indicates the ratio of SiO_2 + Al_2O_3 to the sum of the alkali oxides (R_2O) in the M-Area sludge + spent filter aid. The cross hatched parallelogram represents the known glass forming region in this system while the larger shaded parallelogram represents the extended glass forming region determined in this study by use of reactive silica additives.

To date the TCLP leaching procedure has been performed on one borosilicate glass (M-6) and one SLS glass (M-9). Both of these glass formulations contained 70 wt% waste on a dry basis (Table 1). Both glass formulations had melted to a homogeneous glass at 1150°C. Both glasses passed the TCLP leachate limits for Pb, Ba, and Cr. The borosilicate glass formulation was superior to the SLS glass formulation for

retention of Ni and U (Table 3). The SLS glass (M-9) did not meet the Land Disposal Restrictions for Ni but the borosilicate glass (M-6) did.

Table 3. Toxicity Characteristic Leaching Procedure (TCLP) and land disposal restriction (LDR) limits and response for M-Area glasses.

Element	Wt% Sludge	Wt% Glass M-6[1]	Wt% Glass M-9[1]	Waste Code	LDR Limit (ppm)[2]	TCLP Leachate M-6 (ppm)	TCLP Leachate M-9 (ppm)
Pb	0.10	0.074	0.074	F006	0.51	<0.2	<0.2
Ba	0.018	0.013	0.013	N/A	100	1.85	1.40
Ni	0.73	0.51	0.51	F006	0.32	0.17	0.74
Cr	0.007	0.005	0.005	F006	5.2	<0.04	<0.04
U	2.65	1.85	1.85	N/A	N/A	0.10	0.45

[1]M-6 and M-9 contained 70 wt% waste on a calcine oxide basis
[2]40 CFR 148, et al., Land Disposal Restriction for Third Third Scheduled Wastes Final Rule, 55 CFR 22 250, June 1, 1990.

Incinerator Ash/Incinerator Blowdown Glasses

Reactive silica was added to the CIF incinerator wastes as the only glass forming additive. Mixtures of silica with CIF blowdown and mixtures of silica with CIF blowdown and bottom kiln ash are examples of RASP stabilization. A simulated waste formulation for both the ash and the blowdown indicated that the blowdown was high in Na while the bottom kiln ash was high in Ca and Zn. The high Na_2O and CaO content of this waste indicated that stabilization in SLS glass was feasible by addition of only one additive, SiO_2. The use of only one additive simplifies processability of the waste as only two components need to be adjusted in order to optimize processability and waste loading. All vitrification was conducted at 1150°C to minimize volatility of chlorides and radioactive Cs which will be present.

A waste loading of 45-50 wt% (on a dry oxide basis), which corresponds to a volume reduction of 94%, was demonstrated for solidification of CIF blowdown in soda-lime-silica (SLS) glass. The use of reactive SiO_2 additives in the form of precipitated SiO_2, Perlite (Perflo), diatomaceous earth, and pyrolyzed rice husk ash were shown to improve the solubility of the hazardous and heavy metal constituents in the glass (Table 4). The glasses made with Perlite and diatomaceous earth were easier to fabricate and poured more easily at 1150°C than the glasses made with precipitated SiO_2 and rice husk ash. Mixtures of incinerator blowdown and bottom kiln ash, at known production ratios, were also vitrified (Table 4). Changes in the composition of the CIF wastes can be easily compensated for by adjusting the ratio of the SiO_2 additive to the amount of waste (Figure 3). The SLS glass was shown to be tolerant of a wide range of variability in the waste composition (Table 4). The high ZnO content of the waste, especially of the bottom kiln ash, stabilizes the glass against crystallization and is known to improve glass durability. For the CIF wastes, Figure 3 demonstrates that the use of reactive silica, in this case the spent filter aid already a part of the waste, extends the known glass forming region in the SLS system.

Table 4. Glass Formulations and Additives for CIF Blowdown and CIF Blowdown with Bottom Kiln Ash at 1150°C.

Glass	Waste Loading (wt%)	Amount of Blowdown* (wt%)	Amount of Kiln Ash (wt%)	Type of Additive	Additive Amount (wt%)	Results
CIF-1	50	50	0	SiO_2**	50	Yellow Phase
CIF-2	33	33	0	SiO_2	67	Yellow Phase
CIF-3	30	30	0	SiO_2	70	Yellow Phase
CIF-4	45	45	0	DIATOM EARTH	55	Homogeneous
CIF-5	45	45	0	PERLITE	55	Homogeneous
CIF-6	45	45	0	SiO_2	55	Yellow Phase
CIF-7	50	34	16	SiO_2	50	Yellow Phase
CIF-8	50	50	0	Borosilicate Frit 165	50	Some Cu hydroscopic
CIF-9	45	45	0	PPT SiO_2	55	Homogeneous
CIF-10	50	34	16	DIATOM EARTH	50	Homogeneous
CIF-11	50	34	16	PERLITE	50	Homogeneous
CIF-12	50	34	16	PPT SiO_2	50	Homogeneous
CIF-13	50	50	0	DIATOM EARTH	50	Homogeneous
CIF-14	50	50	0	PPT SiO_2	50	Homogeneous would not pour
CIF-15	33	33	0	PPT SiO_2	67	Homogeneous would not pour
CIF-16	30	30	0	PPT SiO_2	70	Homogeneous would not pour
CIF-17	50	34	16	DIATOM EARTH	50	NaCl-incomplete reaction in 4 hrs.
CIF-18	50	50	0	DIATOM EARTH	50	NaCl-incomplete reaction in 4 hrs.
CIF-19	50	50	0	RICE HUSK SiO_2	50	Did not melt until 1200°C
CIF-20	34+16	34	16	RICE HUSK SiO_2	50	Did not melt until 1200°C

*on a dry weight oxide basis
**SiO_2 refers to granular SiO_2

The SRTC modified EPA TCLP leaching procedure was performed on three homogeneous CIF SLS glasses (CIF-10, 13, 14) and on one of the incompletely reacted CIF SLS glasses (CIF-17). The composition of these glasses is shown in Table 5. Glasses CIF -10 and CIF-17 were vitrified with diatomaceous earth. Both contained mixtures of CIF blowdown and ash at a total waste loading of 50 wt%. Glasses CIF-13 and CIF-14 were vitrified with diatomaceous earth and precipitated SiO_2, respectively. Both were fabricated from 50 wt% dry calcined blowdown. All of the glasses met the LDR leachate limits for Pb, Ba, and Ni (Table 6). The glasses made with diatomaceous earth stabilized the Cr at LDR limits lower than those required for D007 and F006 wastes but not for U032 wastes. The glass made with precipitated SiO_2 met all the LDR limits.

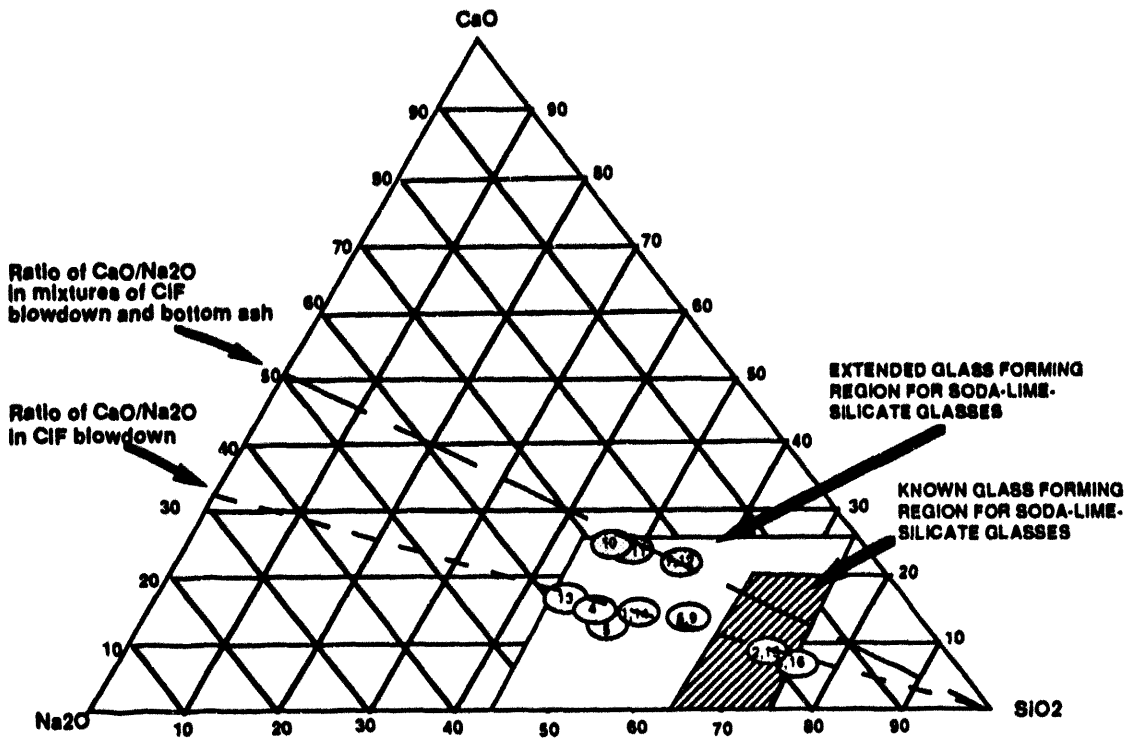

Figure 3. Ternary phase diagram for the system Na_2O-CaO-SiO_2 system with glasses formulated for the CIF wastes superimposed (wt%). The cross hatched parallelogram represents the known glass forming region in this system while the larger shaded parallelogram represents the extended glass forming region determined in this study by use of reactive silica additives.

Table 5. Concentrations of hazardous constituents in the waste glass.

Element	Wt% Blow Down	Wt% Ash	Wt% Diatom Earth*	Wt% Glass CIF-10**	Wt% Glass CIF-13"	Wt% Glass CIF-14"	Wt% Glass CIF-17**
Pb	0.19	0.46	0.18	0.23	0.05'	0.09	0.03'
Ba	0.09	0.22	0.03	0.08	0.06'	0.04	0.08'
Ni	0.00	0.00	0.24	0.13	0.13	0.00	0.13
Cr	0.07	0.17	0.00	0.05	0.03	0.03	0.04'

*Diatomaceous earth used as a glass forming additive for CIF-10, CIF-13 and CIF-17, precipitated silica used as a glass forming additive for CIF-14

**CIF-10 and CIF-17 contained 16 wt% bottom ash and 34 wt% dry blowdown on a calcine oxide basis t measured by Inductively Coupled Plasma Spectroscopy

"CIF-13 and -14 contained 50 wt% dry blowdown on a calcine oxide basis

Table 6. Toxicity characteristic leaching procedure (TCLP) and land disposal restriction (LDR) limits and response for CIF

Element	Waste Code	LDR Limit* (ppm)	CIF-10 Leach (ppm)	CIF-13 Leach (ppm)	CIF-14 Leach (ppm)	CIF-17 Leach (ppm)
Pb	D008	5.0	<0.2	<0.2	<0.2	<0.2
	U051	0.51				
	F006	0.51				
Ba	D005	100	2.2	2.3	2.2	5.12
Ni	F006	0.32	0.15	0.072	N/A[1]	<0.05
Cr	D007	5.0	0.93	0.68	<0.04	0.69
	U032	0.094				
	F006	5.2				

*40 CFR 148, et al., Land Disposal Restriction for Third Third Scheduled Wastes Final Rule, 55 FR 22 250, June 1, 1990
[1]not applicable since no Ni was present in the CIF-14 glass which was made with precipitated silica rather than diatomaceous earth

WASTE MINIMIZATION

Wastewater treatment of M-Area supernate reduces the 1,200,000 gallon volume of the M-Area sludge + supernate by 65-70 volume % leaving 210,000 gallons of sludge and 450,000 gallons of newly created spent filter aid (Table 7). The 210,000 gallons of sludge is approximately 38 wt% dry solids with NO_3 accounting for 4 wt%, at a density of 1.26 kg/L. Evaporation of the NO_3 during vitrification would, therefore leave ~ 34 dry wt% sludge solids remaining for incorporation into glass. The 450,000 gallons of spent filter aid is 17 wt% solids with a density of 1.1 kg/L. Assuming a 75 wt% waste loading, the combined 650,000 gallons of sludge and spent filter aid can be solidified into ~92,000 gallons of glass. This is a sludge/spent filter aid waste volume reduction of ~86% assuming a glass density of 2.7 kg/L for the final glass. Similarly, a 90 wt% waste loading will yield 75,000 gallons of glass and result in an overall waste volume reduction of ~88 volume %.

Table 7. Comparative volume reductions for M-Area waste stabilization.

Stabilization Options	Volume Reduction*
Base Case (cement with supernate) 1,200,000 gallons of M-Area supernate + sludge = 2,400,000 gallons cement	0%
Option 1 (cement without supernate) 650,000 gallons sludge + spent filter aid + cement = 1,300,000 gallons cement	46%
Option 2 (FIST) 650,000 gallons wastewater treated sludge/spent filter aid + cement = 325,000 gallons cement	86%
Option 3 (RASP)** 650,000 gallons wastewater treated sludge + spent filter aid = 92,000 gallons glass	96%

*Relative to original 2,400,000 gallons grout projected if the sludge is not wastewater treated
**Assumes the glass is 75wt% waste on a dry calcine basis

Comparisons of the overall waste volume reduction compared to alternative stabilization strategies in cement (Table 7) shows that vitrification of M-Area sludge and spent filter aid (Option 3) reduces the stabilized

volume by 96% relative to the base case cement stabilization where both supernate and sludge would have to be stabilized. Vitrification of wastewater treated sludge and spent filter aid (Option 3) reduces stabilized volume by an additional 50 volume % relative to Option 1 (cement stabilization of wastewater treated sludge and spent filter aid) and by an additional 10 volume % relative to Option 2 (FIST stabilization (7,8) in cement).

The Consolidated Incinerator Facility (CIF) will create approximately 250,000 gallons of blowdown per year. Eighty-five percent of the blowdown is water and 10 wt% is NaCl solids and ash residue. Some of the anionic constituents, such as Cl are volatile leaving ~8wt% solids to be solidified. A 50 wt% waste loaded SLS glass could be formed from CIF blowdown by adding ~8 wt% SiO_2 to the calculated 8 wt% blowdown residue on a dry basis. Assuming a 50% waste loading and a glass density of 2.7 g/cc, one can project that 250,000 gallons of CIF waste slurry a year will produce ~ 15,000 gallons of glass per year. Stabilization of the CIF blowdown in a 50% waste loaded glass will yield a 94% volume reduction.

The base case stabilization methodology for the CIF blowdown is to immobilize the untreated blowdown in cement. This base case methodology would create a projected 500,000 gallons of cement per year (Table 8). If the CIF blowdown were wastewater treated prior to cement stabilization, 100,000 gallons of cement would be created per year (Option 1). If the CIF blowdown is evaporated to dryness and then solidified in cement, asphalt, bitumen, polymer, etc., 60,000 gallons of stabilized sodium salt and ash solids containing organics would be created (Option 2). Vitrification would create only 15,000 gallons of glass (Option 3).

Table 8. Comparative volume reductions for CIF blowdown waste stabilization in glass compared to cement stabilization, wastewater treatment/stabilization, and evaporation/stabilization.

Stabilization Options	Volume Reduction/year*
Base Case 250,000 gallons/year of CIF blowdown + cement = 500,000 gallons cement/year	0%
Option 1 50,000 gallons wastewater treated CIF blowdown + cement = 100,000 gallons cement/year	80%
Option 2 30,000 gallons CIF blowdown evaporated to dryness + thermoplastic resin = 60,000 gallons stabilized evaporate/year	88%
Option 3 (RASP) 250,000 gallons CIF blowdown = 15,000 gallons glass/year	97%

*Relative to original 500,000 gallons grout/year projected for the base case.

Comparison of vitrification of CIF blowdown to the alternative stabilization in concrete (Table 8) demonstrates that a 97% volume reduction can be realized compared to stabilization of unevaporated blowdown in concrete (Base Case). An additional 17% volume reduction can be achieved compared to the alternative of wastewater treatment coupled with cement stabilization (Option 1), and a 9% reduction compared to the alternative of evaporation and stabilization (Option 2).

CONCLUSIONS

Laboratory scale studies have demonstrated that vitrification of hazardous/mixed wastes at the SRS is viable for (1) nickel plating line (F006) sludges and (2) incinerator wastes. Vitrification of these wastes using high surface area additives, the RASP, was shown to enhance the dissolution and retention of hazardous, mixed, and heavy metal species in glass. Vitrification has been achieved in both soda-lime-silica and borosilicate glasses at waste loadings from 50 (CIF wastes) to 90 (sludge wastes) wt%. These waste loadings correspond to volume reductions of 94% and 86%, respectively, with large associated savings in storage costs.

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PILOT SCALE VITRIFICATION STUDIES ON HAZARDOUS AND MIXED WASTES

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ABSTRACT. Clemson University Environmental Systems Engineering, in cooperation with research partners Westinghouse Savannah River Company, EnVitCo, Inc., and Stir-Melter, Inc., has established a center for pilot scale waste vitrification research. The purpose of the center is to conduct vitrification feasibility studies and environmental impact studies on various defense and industrial hazardous and mixed wastes.

Treatability studies are being conducted on several hazardous wastes and surrogates of hazardous and mixed wastes. Tests include treatment of contaminated concrete, wastewater treatment sludges, ion exchange resins, incinerator ash, and electronic circuit boards. The program will include tests to control precious metal separation and organic destruction as an integral part of the melter operation, while incorporating heavy metals into the glass matrix.

Each test program will include characterization of the untreated wastes and residual glasses, both by total constituent analysis and Toxicity Characteristic Leaching Procedure (TCLP). Offgases will also be studied for the degree of organic combustion, particle emissions, metal volatility, and semi-volatile organic emissions.

INTRODUCTION

Over the past 30 years, the U.S. Department of Energy (DOE) has committed extensive resources to the development of technologies suitable for the stabilization of high level radioactive waste. The objective of this work is to produce a vitreous wasteform capable of retaining the radioactive fractions in a leach resistant form. This vitrified waste will be disposed of in deep, subsurface repositories, where it will remain geologically isolated. Vitrification is the preferred method of stabilization for the DOE's high level waste, and has also been chosen for treatment of high level wastes in Germany, France, Great Britain, and Japan (1).

Vitrification involves the conversion of solid- or liquid-based wastes into a glass residual form by heating the waste and appropriate glass forming additives to the point of fusion. The process results in the destruction, removal, and/or permanent immobilization of the hazardous components. The final wasteform is a solid, highly leach-resistant glass, which is of high environmental integrity and is often of lower volume than the original waste. The advantages of vitrification over other stabilization methods include the improved stability of the wasteform and the decreased disposal costs due to reduced waste volume.

In an effort to further the development of technologies based within the DOE complex, the DOE is making efforts to promote technical transfer initiatives that will bring these technologies to the private sector. To this end, the DOE through the Savannah River Site is working with Clemson University's Environmental Systems Engineering Department to establish a laboratory dedicated to vitrification research. The laboratory is part of a cooperative effort which was initiated September, 1992 between Westinghouse Savannah River Company, Clemson University, and their industrial partners EnVitCo, Inc., and Stir- Melter, Inc.

This paper reports on the capabilities of the laboratory and gives results from the test on the vitrification of simulated nickel plating sludge.

FACILITIES AND MELTING CAPABILITIES

The laboratory is a dedicated, 2000 ft^2 facility co-located with the Clemson University's Rich Environmental Research Laboratory. The vitrification laboratory houses two melters, offgas treatment system, feed preparation equipment, and system monitoring and sampling equipment.

Melters

The melting capabilities include a cold top, high-temperature, joule heated melter manufactured by EnVitCo, Inc., an affiliated company of Toledo Engineering Co., Inc. of Sylvania, OH. The EnVitCo EV-16 is a refractory-lined, water-cooled 0.16 m^2 (0.07 m^3) melter that utilizes the 'cold top' method to reduce metal volatility and heat losses from the molten glass. A diagram of the system is presented in Fig. 1. The cold top principle involves maintaining a layer of cooler feed materials (batch) on top of the molten glass. As the hot glass is drawn off from the bottom of the melter, the layer of batch closest to the molten bath continues to melt, while additional batch is added to the top of the layer. There is a large temperature gradient across this zone, typically ranging from about 1500°C in the molten glass, to about 200°C on the top of the batch. The advantage of this concept in waste vitrification is that the cool batch layer serves as a condensation zone for metals that may volatilize from the molten waste bath. The batch layer also serves to insulate the glass bath, reducing the convective heat losses to the atmosphere in the melter headspace.

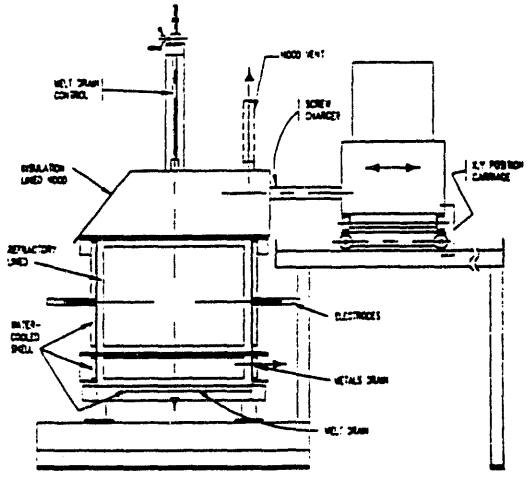

Figure 1. EnVitCo EV-16 Cold Top Melter Module-Cross Section

The EnVitCo unit is also considered a high-temperature melter. The high-temperature capabilities are due to the nature of the melter construction, which utilizes a refractory-lined, water-cooled melting chamber and molybdenum electrodes. The high temperatures help to dissolve waste fractions that require decomposition at higher temperature. In addition, the high temperatures help homogenize the glass mixture both by decreasing the viscosity of the melt and creating convective currents within the melt chamber.

The second melter is a WV-1/4 stirred tank melter, manufactured by Stir Melter, Inc., a subsidiary of Glasstech, Inc. of Perrysburg, OH. The Stir-Melter™ is a 0.022 m^2 (0.007 m^3) system utilizing a unique approach to the joule heating process. This is done through the use of an Inconel™ 601 impeller serving as one electrode, and an Inconel 601 vessel serving as the second electrode, as shown in Fig. 2. The energy is then applied through a circuit between the impeller and vessel, while the impeller mixes the glass at high rates. Mixing characteristics can be controlled by varying the speed and height of the impeller relative to the depth of the glass. At high mixing rates the glass becomes entrained with air and hot gases from the melt, and takes on a foamy character with reduced viscosity. The high mixing rates and lower viscosity permit rapid incorporation of the batch materials into the melt (2).

The Stir-Melter system has secondary heating capacity available through resistance heating coils surrounding the vessel. This secondary system is capable of initially melting glass cullet and supplying sufficient energy to maintain a molten bath in the event that the stirring system is not used. Once the molten bath is established, the operator has the choice of running the system using the secondary heating system, the joule heating system, or a combination of the two. To initiate joule heating, the operator need only lower the impeller into the molten bath, and apply power to the joule heated circuit between the impeller and vessel.

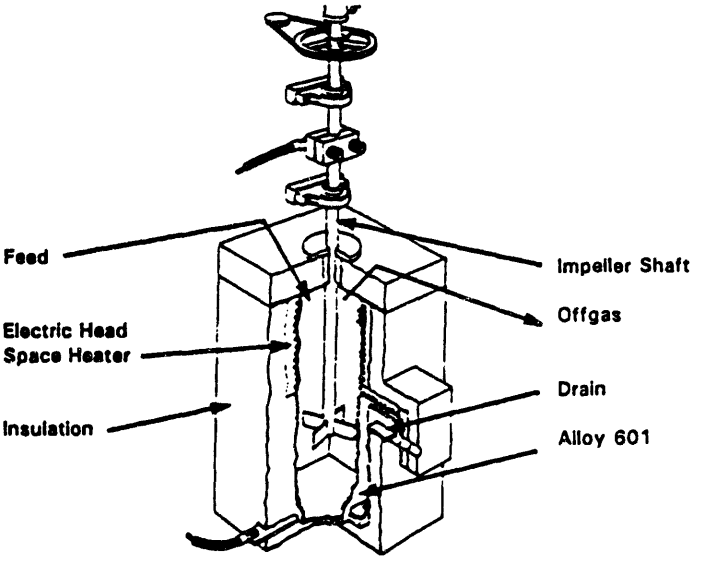

Figure 2. Stir-Melter WV-0.25 Stirred Tank Melter

In addition to the two melters at the Clemson laboratory, the program also has access to additional melting facilities, as indicated in Fig. 3. Through the South Carolina Research Authority (SCRA), Clemson University can lease access to a 1 MW plasma arc melting system located in Charleston, SC. This is a transferred arc system that was built through an agreement between the SCRA and the Massachusetts Institute of Technology (MIT). Though there is no current plan to utilize this system over the near term, the unit is available. Savannah River Site also operates a batch-type Induction Melter that will be used in support of the work conducted at Clemson. This system offers a range of operating capabilities, including melt temperatures between 500 to 1800°C and widely variable redox conditions. This flexibility allows for processing strategies which permit control of metals separation, metal volatility, and organic destruction.

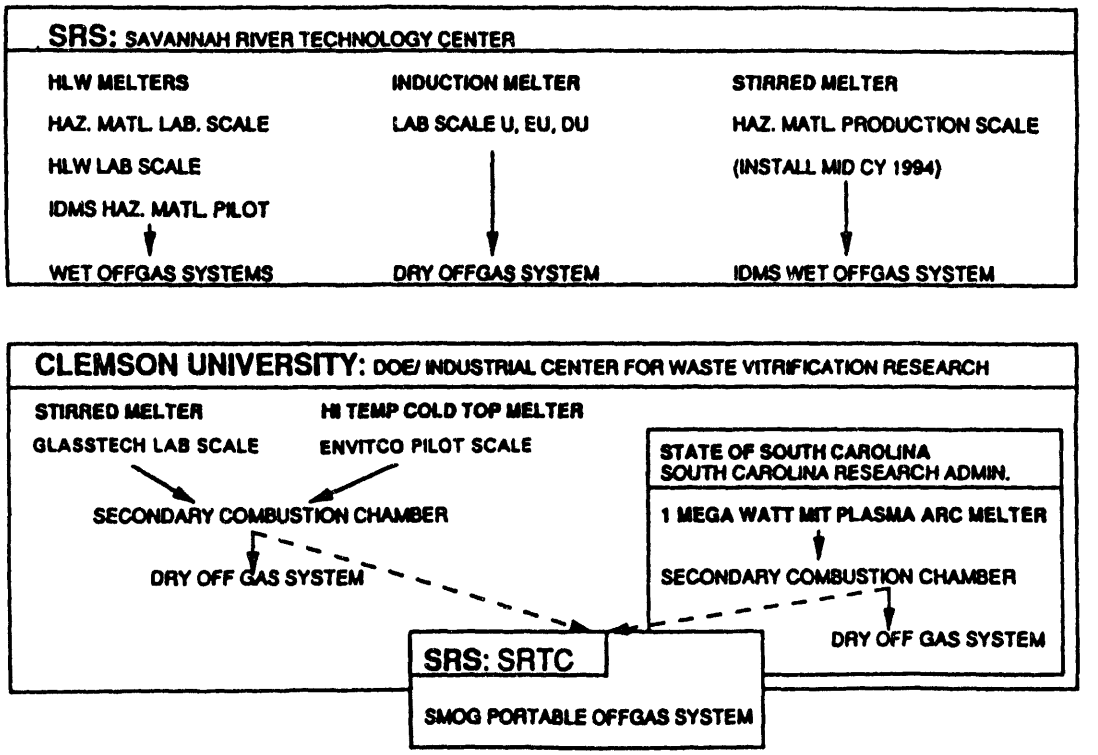

Figure 3. Available Hazardous Waste/Mixed Waste Melter Systems

Offgas

The offgas treatment system is designed to destroy volatile organics and remove particles that escape from the melter. The facility is serviced by a negative pressure central header with drops to the individual machines. A propane fired secondary combustion chamber destroys most volatile organics. The chamber is designed for residence times of 0.2 to 0.5 s (depending on system flow requirements) at a temperature of 1200°F. Following the secondary combustion chamber is an air dilution/spray quench chamber that cools the afterburner gases and allows for control of the melter headspace pressure drop and flow rates through the afterburner. After cooldown, the gases are routed through a multi-media packed-bed filter system. The filter is filled with a combination of fiberglass and sand, staged in a manner to maximize their filtration capacity while minimizing pressure losses across each stage. This unit is designed to serve as a prototype for a high temperature media filter, which will be capable of treating hot offgases directly off the melters

or from the secondary combustion chamber. All media used in this unit are selected on their ability to be recycled back into the vitrification unit as a glass-forming additive. The fiberglass and sand media currently being used can be processed without much difficulty in either melter system. To assure minimal losses during testing and development of the packed-bed filter, the offgases receive a final treatment through high efficiency particulate air (HEPA) filters. The system is driven by a rotary blower which supplies a vacuum through all points of the offgas train. This reduces the potential for gases escaping into the laboratory.

The Vitrification Laboratory is currently limited on types and chemistries of waste that can be processed due to the design of the offgas treatment system. The current offgas treatment train is designed to handle organic fumes and particulate. As the program has developed, the system limitations have been realized, and are being addressed. This includes upgrading of the entire offgas system to stainless steel construction to handle acid gases generated by chloride, sulfate and nitrate ions in the wastestreams. The secondary combustion chamber is being redesigned to increase destruction capacity through longer residence times and higher temperatures. Though no PCB contaminated wastes are planned at this time, some consideration will be give to polychlorinated biphenyls (PCB) destruction in the redesign. In addition, offgas scrubbing and neutralization will be added to the treatment train to remove acid gases and further reduce particulate emissions. The upgraded system should be operational by September, 1993.

No low level radioactive wastes are planned for testing in the near term. This decision is driven by the economics and management issues associated with the handling of radioactive waste. Radioactive tracers and short half life isotopes may be used for tracer testing or to demonstrate capture efficiencies in surrogate melt studies.

OPERATING AND PERMITTING ISSUES

Treatability Studies

South Carolina is authorized by the U.S. Environmental Protection Agency (EPA) to administer its own hazardous waste regulatory program. This program is administered by the Department of Health and Environmental Control (DHEC) in accordance with the South Carolina Solid and Hazardous Waste Act. Due to the variable nature of the surrogates and waste streams to be handled at the facility, the samples will be handled in accordance with the requirements for treatability studies. Essentially, by complying with the limitations imposed by the treatability study regulations, the samples handled at the site are excluded under 261.4 (e), (f) (3). These regulations allow exemptions from 40 CFR 124, 262-266, 268, and 270 (4-11). Under the title of treatability studies, the site is required to operate under certain storage and processing restrictions, as described in 40 CFR 261.4 (f) (3).

South Carolina DHEC was notified in September of 1992 of the intention to commence treatability studies and granted permission to proceed. All waste streams from the experimental process will be analyzed by the TCLP to determine the toxicity characteristics. The wastes will then either be returned to the generator under 261.4 (e) (3), or will be disposed of in an appropriate facility after consultation with the DHEC Waste Assessment Branch.

Based upon the definition of vitrification as thermal treatment rather than incineration, an operating vitrification treatment facility would likely be permitted under Subpart X of 40 CFR 264 (7) (Permit Standards for Miscellaneous Units) and Subpart P, Part 265 (8) (Interim Status Standards). Subpart X facility requirements are not specific, but instead direct that applicable requirements from Subpart I through Subpart O of Part 264 (7) be followed as appropriate to the unit (12).

Air quality

Clemson University submitted an application to the SC DHEC Bureau of Air Quality control for a Part IIB (Process Application) air quality permit. The South Carolina Air Quality regulations allow exemption from the permitting under a variety of conditions. Due to the small size of the facility, the estimated emissions based on the project schedule were assessed to be below the limit typically requiring a permit. DHEC has granted a conditional exemption for air permitting based on the low levels of projected emissions (12).

TEST PROGRAM

Two objectives in the development of the Clemson Vitrification Laboratory are to support the efforts of the DOE in technology development and transfer, as well as demonstrate the capabilities of commercially available melting equipment. Clemson serves as an independent site, capable of conducting full characterization studies of the wastestreams, melting systems, offgases and final glass wasteform.

One of the primary focuses includes treatability studies designed to demonstrate vitrification technologies as alternative hazardous waste treatment methods to cementation, polymerization and other conventional methods. To this end, Clemson is developing a testing program that will generate data and information that may be used to support 'process based' delisting petitions for some listed hazardous wastes. To strengthen the validity of data and assure that the proper analytical quality control methods are utilized, the program includes use of EPA recognized laboratories for all tests and data that are considered critical to the process demonstration and desisting efforts. This includes waste/surrogate composition verifications, glass wasteform composition, offgas volatile and particulate analysis, Product Consistency Testing (PCT), and EPA's Toxicity Characteristic Leaching Procedure (TCLP).

To complete mass balance calculations, wastes/surrogates will be tested for organic content by Loss on Ignition (LOI), and inorganic composition by acid digestion followed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and/or atomic absorption (AA) analysis. Anion concentrations will be determined by ion chromatography (IC). Offgases will be sampled for particulate matter by EPA Method 5, semivolatile organics by EPA Modified Method 5, and volatile metals by Multiple Metals Sampling Train (MMST) based on EPA Method 12 (MMST as EPA Draft Method 29). Particle size distribution will be determined by cascade impactor analysis. Particulate matter from either the impactor sampling or the Method 5 sampling will be digested and analyzed for inorganic and anion concentrations.

Preliminary tests have been conducted to observe the performance of the EnVitCo melter and the offgas treatment system, as well as address some of the operating issues such as surrogate preparation, surrogate feeding, processing rates, etc. The first waste tested was a surrogate of wastewater treatment sludge from nickel plating operations. The actual waste is produced after the plating bath solution has been flocculated and precipitated, and the supernatant has been decanted and fine-filtered through a precoat filter. The precipitate and precoat media are then combined, and form a sludge of metal hydroxide precipitates, diatomaceous earth and perlite filter aids, nitrate, water, and low levels of chlorine, sulfate, and fluoride. The composition of the dry feedstock tested is summarized in Table 1.

A sample of the glass produced was tested by a commercial laboratory using the TCLP for RCRA regulated metals. The results from this test, along with the present TCLP limits for characteristic wastes and the Land Disposal Regulation levels for F006 listed wastes are presented in Table 2.

TCLP data for the vitrified wasteform indicates performance well within the standards set for characteristic wastes, with leachate metal concentrations typically one to two orders of magnitude below the required limits. This performance is satisfactory for handling and Subtitle D (non-hazardous) disposal of the glass as manufactured from surrogate feedstock.

Table 1. Surrogate Formulation (Dry Basis) for Nickel Plating Filter Sludge.

Oxide	Surrogate Oxide Composition, Wt %	Final Batch Composition, Wt %
SiO_2	54.334	36.571
Al_2O_3	21.768	14.652
B_2O_3	0.040	24.595
Na_2O_3	13.513	17.220
K_2O	1.847	1.243
MgO	0.248	0.167
CaO	0.593	0.399
BaO	0.035	0.024
Cr_2O_3	0.018	0.012
CuO	0.031	0.021
Fe_2O_3	1.105	0.744
MnO	0.354	0.238
NiO	1.158	0.780
PbO	0.134	0.090
ZnO	0.729	0.491
P_2O_5	4.028	2.711
TiO_2	0.062	0.042
Total	100.000	100.000

No conclusion can be drawn as to whether the performance is acceptable relative to LDR levels, since the required concentrations are typically below the sensitivity range of the analytical method. Information on the leaching of nickel is not available since the standard TCLP test is only concerned with RCRA controlled metals, and nickel analysis was not requested. Although the surrogate is formulated to represent a listed waste, vitrified residues of actual F006 wastes would be required to meet the LDR limits listed.

The sensitivity of the AA methods used to determine the metal concentrations in the TCLP leachate is inadequate to draw any conclusions about whether the glass meets LDR requirements. Determination of LDR conformance will require a second evaluation of the TCLP leachate using a more sensitive analytical method such as ICP-AES. Followup testing will include a re-evaluation of the glass to determine if it meets the LDR requirements, and a repeat of the test using the stirred tank melter with the same surrogate formulations. Additional tests are planned to determine the affects of slurry feeding of the waste, offgas characterization for both dry feed and slurry feeding, and mass balance determinations.

CONCLUSIONS

A laboratory for vitrification research has been established at Clemson University. The laboratory has a 0.16 m^2 cold top melter manufactured by EnVitCo, Inc., and a 0.022 m^2 stirred tank melter manufactured by Stir Melter, Inc. The laboratory, funded by the U. S. Department of Energy, is a cooperative effortbetween Westinghouse Savannah River Company and Clemson University and their industrial partners, EnVitCo, Inc. and Stir Melter, Inc.

Tests have been conducted on the vitrification of a surrogate nickel plating wastewater sludge with the cold top melter. The waste glass produced was tested using the TCLP test, simulating the potential for leaching

of regulated metals in a landfill. The concentrations reported were far lower than the characteristic limits for hazardous waste. Since the actual waste is a listed hazardous waste, its vitrified residues must meet more rigorous land disposal restrictions prior to disposal in a hazardous waste landfill. Due to the sensitivity limits of the TCLP test performed, no conclusion can be made if the waste glass from this surrogate tests met these land disposal limits.

Table 2. Glass Performance Against TCLP and LDR Leachate Levels

Waste Code	Regulated Metal	RCRA TCLP[a] Limit (mg/L)	RCRA LDR[b] Limit (mg/L)	TCLP Test Data (mg/L)
Characteristic Waste Codes				
D004	Arsenic	5.0	5.0	< 0.04
D005	Barium	100.0	100.0	< 1.
D006	Cadmium	1.0	1.0	< 0.1
D007	Chromium	5.0	5.0	< 0.5
D008	Lead	5.0	5.0	< 1.
D009	Mercury	0.20	0.20	< 0.002
D010	Selenium	1.0	5.7	< 0.04
D011	Silver	5.0	5.0	< 0.2
Listed Waste Codes				
F006[c]	Cadmium	1.0	0.066	< 0.1
F006	Chromium	5.0	5.2	< 0.5
F006	Lead	5.0	0.51	< 1.
F006	Nickel	N/A	0.32	N/A
F006	Silver	5.0	0.072	< 0.2

[a] TCLP: Maximum concentration of contaminants (40 CFR 261.24; see 55 FR 11862, March 12, 1990) as determined by Toxicity Characteristic Leaching Procedure.
[b] LDR: Concentration based standards for Land Disposal Requirements, (40 CFR 268.41 and 268.43).
[c] F006: Hazardous Waste from Non-Specific Sources; Wastewater treatment sludges from electroplating operations.

Future tests will be conducted. These tests will simulated wastewater sludges from a number of Department of Energy facilities. The tests will include sampling of the offgases to determine the magnitude of the air emissions.

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CHAPTER 5

Characterization

AN APPROACH FOR SAMPLING SOLID HETEROGENEOUS WASTE AT THE HANFORD SITE WASTE RECEIVING AND PROCESSING AND SOLID WASTE PROJECTS

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ABSTRACT. This paper addresses the problem of obtaining meaningful data from samples of solid heterogeneous waste while maintaining sample rates as low as practical. The Waste Receiving and Processing Facility, Module 1, at the Hanford Site in south-central Washington State will process mostly heterogeneous solid wastes. The presence of hazardous waste is documented for some packages and unknown for others. Waste characterization is needed to segregate the waste, meet waste acceptance and shipping requirements, and meet facility permitting requirements. Sampling and analysis are expensive, and no amount of sampling will produce absolute certainty of waste contents. A sampling strategy is proposed that provides acceptable confidence in waste characterization with achievable sampling rates.

INTRODUCTION

The Hanford Site, located in south-central Washington State, has a variety of forms of radioactive and mixed waste to be treated and/or disposed. The Waste Receiving and Processing Facility Module 1 (WRAP-1) currently is being designed to examine, process, certify, and ship drums and boxes of solid wastes that have a surface dose rate of less than 200 mrem/h. These wastes, known as Contact Handled (1), consist of both waste currently in retrievable storage and waste to be newly generated concurrently with the operation of WRAP-1. WRAP-1 will segregate the waste into three streams. Transuranic (TRU) waste, which contains greater than 100 nCi of transuranic radionuclides per gram of waste matrix, will be packaged and certified for shipment to the Waste Isolation Pilot Plant (WIPP) in New Mexico (2,3) in accordance with WIPP acceptance criteria (4). Waste below this limit containing dangerous waste, as defined by Washington State Administrative Code 173-303 (5), will be held for subsequent treatment at another facility. Dangerous waste is a term used by Washington State to include wastes defined as hazardous under the Resource Conservation and Recovery Act (RCRA) (6) and other wastes regulated by Washington State. Waste below the 100 nCi/g limit, which is free of dangerous waste, is considered low-level waste (LLW) (1) and will be disposed of onsite.

The proper characterization of waste is driven by several needs. These needs include: the designation of the waste for subsequent treatment and/or disposal, waste acceptance requirements for disposal at WIPP or at the Hanford Site, documentation required for shipping of the waste, and the permitting requirements for operation of the facility.

The most challenging waste to be characterized is the retrievably stored waste. There are nearly 38,000 drums of retrievable waste buried in trenches (7).

Characterization of the waste for each drum will include several steps. These steps include examination and weighing of the drum, Non-Destructive Assay (NDA), Non-Destructive Examination (NDE) through real-

time radiography, and chemical analysis of a head-gas sample. These steps, in combination with the available waste history, will answer many, but not all, questions needed to characterize the waste. Some physical sampling and analysis of the waste will be needed to identify dangerous wastes that are not able to be identified through any of the other characterization steps.

Sampling large quantities of heterogeneous waste presents an important challenge. Taking many samples, with analysis done to meet certification requirements, becomes very expensive and increases personnel exposure to radiation. However, no amount of sampling will produce absolute certainty of the content of this waste. This paper will consider the problem of how to provide acceptable levels of confidence with achievable sampling rates.

RETRIEVABLE WASTE DESCRIPTION

The U.S. Atomic Energy in 1970 defined TRU waste as a separate waste category and required that it be stored in a retrievable form, pending decisions on permanent disposal (8). At that time, 10 nCi/g was selected as the lower limit for the TRU waste category. Waste with a TRU content above that limit was stored in the Hanford Site burial grounds. The limit was revised upward to the present value of 100 Ci/g in 1982 (7). Equipment required to assay to the 100 nCi/g limit was installed in 1985 (7). Some waste stored between 1970 and 1985 will be found to be below the TRU limit when it is retrieved and assayed. It has been estimated that 47 percent of the 37,641 drums in retrievable storage will be found to be LLW when assayed (7).

Waste continued to be buried in this form through 1988. This waste is from 44 different sources, both onsite and offsite. The waste comes from processing operations of several types such as cleanup operations, laboratories, and other sources. It can include metal, gluss, wood, paper, cloth, liquid, powder, etc. Most of the waste is heterogenous in nature. Most drums contain multiple packages of waste within plastic bags.

The older the waste, the less information there is available on it. In particular, documentation of the dangerous waste constituents is incomplete for the older waste. Generators have been required to document the presence of dangerous constituents in the waste since 1986 (7). Prior to that, limited information is available on the presence of dangerous constituents in the retrievable waste. Consequently, just over 2 % of the retrievable drums are currently documented as containing dangerous waste constituents. However, it is estimated that approximately 12 % of all drums will contain some dangerous waste constituents. This estimate is based on the percentage of drums with mixed waste received between 1986 and 1988, after generators were required to document mixed waste.

Some of the dangerous waste constituents will be detected through head gas analysis. Some will be in a form, such as discarded lead shielding, that is detectable through NDE. NDE will also identify smaller containers within the drums. These containers will contain some of the dangerous waste and will be removed from the main process enclosure and processed separately. None of these conditions contribute to the problem of detecting dangerous waste constituents by sampling heterogenous waste. However, some dangerous waste constituents are expected in the heterogenous waste that is not detectable through means other than sampling.

SAMPLING STRATEGY

Following is a strategy proposed for use to determine the amount of sampling needed for characterization in WRAP-1 and the conclusions that will be drawn from that sampling. Prior to actual use, this strategy will need to be approved as part of the RCRA permit and as an element of waste acceptance documentation.

Define Lot

The proposed strategy is based on drums of waste being processed in lots. To be defined as a lot for sampling purposes, a group of drums would need to meet three requirements: (a) the drums, based on what is known about the process that produced them, contain similar waste; (b) the expected probability of finding dangerous waste constituents, through sampling, is equal; and (c) the drums are available for processing through WRAP-1, such that the lot can be dispositioned together. That is, the first drums to be processed must be stored until final conclusions are drawn for the lot. Nonconforming items and dangerous waste constituents that are identifiable through other means will have been dispositioned separately and do not impact the issue addressed by this paper. Process history, waste type, other characterization data (NDE, NDA, Head Gas Analysis), and burial records may all provide information useful in defining lots.

Examples. Out of the 236 drums received from Rockwell Energy Systems Group, there is a 21-drum shipment known to contain oil, based on burial records. There are 7 shipments totaling 93 drums known to contain lead. The 21 drums in which oil is suspected would not be grouped in a lot with the remaining drums unless the oil is containerized, identified through NDE, and removed before sampling. Because lead can be detected through NDE and removed prior to sampling, the 93 drums in which lead is suspected could be included in the same lot unless the waste type for these drums is significantly different.

There are 203 drums received from Exxon and 150 from General Electric. Although these drums are from different generators, they are the result of similar processes and are similar in age. There is a low expectation of finding dangerous constituents in this waste, and it is likely that all 353 drums could be grouped together as a lot.

It should be noted that in both examples, final definition of lots will be done based on additional information that will be available after retrieval.

Minimum Process Sampling and Analysis

Random samples of a lot will be taken until one of following two conclusions is drawn.

1. No dangerous constituents have been detected and the lot can be considered free of dangerous waste. The number of samples needed to draw this conclusion is a function of the variables used in the following statements. "We will be w% confident that lots with x% or less drums containing dangerous waste will be accepted, and we will be y% confident that lots with z% or more drums with dangerous waste will be rejected." These variables are negotiable with regulatory agencies, through the permitting and waste acceptance process, but are expected to result in the need to sample approximately 25 drums (for most lots larger than 100) to consider the lot free of dangerous waste.

2. Some dangerous waste constituents have been detected, but further analysis is needed to draw a conclusion. In this case, the number of samples will not exceed the number that would be required to draw conclusion "a" (approximately 25 drums sampled), but a smaller number of samples will be taken if a high percentage of them contain dangerous waste constituents. This reject number is also a function of the variables in the above risk statements, but it will take approximately two drums found to have dangerous waste constituents to suspend further sampling at this step. Further sampling would only be done after statistical and economic analysis has determined that additional sampling is necessary and cost effective.

Process sampling and analysis will have data quality adequate to make reliable processing decisions, but will be less expensive than the more stringent analysis needed to meet certification requirements of regulatory agencies.

The number of samples per drum will depend upon the data quality objectives, the sampling method, the number of packages of waste in a drum, and the heterogeneity of the waste within a drum. Currently, WRAP-1 is being designed based on a "snip and swipe" sampling method. In this method, small portions of soft waste are removed as samples and hard items requiring sampling have a smear sample taken. These methods lend themselves to "authoritative" sampling within the drum; that is, the waste items in the drum most likely to contain dangerous waste constituents are sampled. The drum will have been selected on a random basis, but the waste items within the drum may be selected on an authoritative basis. Using the snip and swipe method, three to four samples are likely to be taken from each drum sampled. This does not ensure that an unsampled packet within a drum would not contain dangerous waste constituents. Rather, the statistically based sampling approach will be based on confidence statements as described above. Remote detection methods, which would provide near real-time analysis of waste during processing, are being evaluated. If a remote detection method is used for process sampling, it is likely that the number of detections per drum sampled will increase due to the speed and ease with which these readings can be taken.

Dangerous Waste Constituents Detection

Analysis will be completed for dangerous waste constituents that could potentially be in the waste. Process history and other characterization data will be used to rule out constituents that do not require analysis. Only those constituents found at this step will be of further concern if additional process sampling and analysis are required.

Subdivision of Lots

The appearance of dangerous waste constituents in the lot may be able to be correlated to some factor that had not been considered in the initial definition of the lot. For example, if the drums that had dangerous waste constituents in their samples also had pumps or piping in the drums and drums without pumps or piping were free of dangerous waste constituents, this might be used as a basis for subdividing the lot. Based on NDE examination, those drums with pumps and piping could be considered a sublot and those without another sublot. Any information that is available through NDE, NDA, head-gas analysis, process history, or burial records and that also correlates with dangerous waste constituents in the known samples may be used. This is true even if the reason for the correlation is unknown. The sublots will now be handled as separate lots and any additional sampling to meet "minimal" requirements will have to be done.

Example. Suppose a 1,000-drum lot is divided into 203 suspected of containing dangerous waste and 797 are expected to be free of dangerous waste, based on correlation with 5 drums sampled and found to contain dangerous constituents and 20 drums sampled and found to be free of dangerous waste. The previous sample results are applicable to the new lots, but the 797-drum lot will require 5 additional drums to be sampled (for a total of 25). The lot suspected of containing dangerous waste will require consideration to determine if additional sampling is warranted.

Lots With Small Quantities of Dangerous Waste Constituents

If a lot has some dangerous waste constituents and there is no basis for subdividing the lot (there is no basis for predicting the presence of dangerous waste constituents in the drums that have not been sampled), the lot may still qualify as non-dangerous if the amount of dangerous waste constituents is small. Based on EPA SW-846 (9), the lot can qualify as non-dangerous if the confidence interval is less than the regulatory threshold.

Examples. Assume samples are taken from 25 randomly selected drums and 23 are found to have no detectable dangerous waste constituents, but 2 have levels of 250 and 200 ppm, respectively, of a constituent with a regulatory threshold (RT) of 50 ppm. The sample mean would be 18; the variance (s^2) would be

3.933; the standard deviation (s) would be 62.7; the standard error would be 12.5; and the confidence interval (CI) would be 32.5. Because this is below the RT of 50 ppm, the entire lot can be declared non-dangerous based on these samples.

Assume results similar to the previous example, except that the two samples with a dangerous waste constituent have results of 500 and 600 ppm, respectively. In this case, the sample mean would be 44 (still below the RT); the s^2 would be 23,400; s would be 153; the standard error would be 30.6; and CI would be 81.3. Because this is above the RT, the lot cannot be declared non-dangerous without additional sampling.

Consideration of Additional Sampling

In cases where the sample mean is below the RT, but the CI is above the RT, additional sampling may be considered. It is possible that additional sampling will lower the CI, which is a function of the number of samples, sufficiently to declare the lot non-dangerous. Before additional samples are taken, the number that would be needed to qualify the lot as non-dangerous should be estimated. If the sample mean is above the regulatory threshold, there is no reason to expect further sampling to qualify the lot, and a decision must be made whether it is economically justifiable to sample each drum.

Examples. In the previous example where the sample mean is 44, the RT is 50, and the CI is 84.3, consideration should be given to additional sampling as a means of qualifying the lot as non-dangerous. Assume that the number of samples increased until CI < RT. Also, assume that the additional samples have results similar to the initial 25 (i.e., the sample mean and s are unchanged). With the sample mean at 44, reducing CI to below 50 would require an additional 1,043 samples, based on the relationship between CI and the number of samples.

Consider a lot in which 23 of 25 samples contained no detectable dangerous waste constituents and the other two had levels of 350 and 400, respectively, of a constituent with an RT of 50. The sample mean would be 30, and the CI would be 57.4, above the RT. In this case, adding samples with the same sample mean and s would reduce CI below RT after an additional 21 (for a total of 46) samples are taken. The additional samples may change the sample mean and s, which would increase or decrease the actual number of samples required to qualify this lot as non-dangerous.

Before additional samples are taken or analyzed, consideration must be given to the economic justification of the additional sampling and analysis. This will be based on three values: (a) the estimated number of non-dangerous drums in the lot, (b) the cost of the additional sampling, and (c) the added cost of treating non-dangerous waste as dangerous. The last value will depend on the treatment required for the specific waste type and dangerous waste constituent under consideration.

Additional sampling has the potential operational effect of recycling drums through the process enclosure, which were previously processed. In some cases, it may be beneficial initially to take more samples than are needed and perform analysis only on as many as are required.

Extended Lots

In some cases, a lot may have been processed which is expected to be similar to additional drums that are yet to be retrieved. After a lot has been designated non-dangerous, other similar drums can be designated as an extension of the same lot. A representative number of these drums will be randomly sampled to confirm that they are indeed similar to those that have already been qualified. Process sampling and analysis will be done to confirm that an extended lot, which is considered non-dangerous, continues to qualify as non-dangerous on the same basis as the original lot.

Examples. A lot of 100 drums qualifies as non-dangerous based on 25 drums being sampled without any dangerous waste constituents being detected. Another 900 drums are identified as candidates for the same lot had they been available for processing at the same time. These 900 drums, located such that their retrieval will take place over a number of years, will be received at WRAP-1 in groups of 50 or less. For each new group, a number of drums will be randomly selected that would equal a rate of 25 drums over the cumulative number of drums in the extended lot. That is, in a group of 47 received immediately after the first 100 were qualified, 8 drums (25,47/147) would be sampled. In the last group of 40, out of a total of 1,000, only 1 drum (25,40/1000) would be sampled. As long as samples continued to be free of dangerous waste constituents, drums would be dispositioned on an ongoing basis.

In a lot with some dangerous waste constituents that was qualified based on CI<RT, the number of samples from each new group would be selected in the same manner with CI being updated, based on ongoing results.

Combined Lots

After process sampling has occurred, there may be justification for combining lots of non-dangerous waste to reduce the amount of more stringent analysis done to meet regulatory requirements. To justify this step, it would need to be shown that the combined lot consists of similar waste with an equal, very low, probability of finding dangerous waste constituents in a sample.

Sampling Each Drum of a Lot

Some lots that cannot be qualified as non-dangerous through sampling may not have any basis for subdividing the lot. However, there may still be a significant number of non-dangerous drums in the lot. The only way to segregate the non-dangerous drums in this case is to sample every drum. In this case, the purpose of sampling is to categorize the drum without regard to the rest of the lot. Each drum is treated as though it was a separate lot and will be designated as dangerous or non-dangerous based on sample results from that drum.

Before this is done, the cost of the additional sampling must be compared to the cost of treating the entire lot as dangerous waste. An estimated number of non-dangerous drums in the lot will be based on the previous sample results.

After this segregation has occurred, the dangerous and non-dangerous groups may be considered segregated lots and further stringent analysis needed may be applied to these segregated lots.

Analysis to Meet Regulatory Requirements

The data quality and the amount of documentation needed for waste certification to satisfy regulatory agencies are expected to be greater than are needed for processing decisions. The number of samples taken for certification can be minimized by considering process sampling as part of the process that produces a final lot for certification purposes. The final lot can be based on the original lot, an extended lot, a combined lot, or a segregated lot.

CONCLUSION

The anticipation of success with the above sampling strategy is based on estimates that there will be a significant number of lots processed by WRAP-1 without dangerous waste constituents in the samples, and a relatively small number of lots that will warrant drum-by-drum segregation. There are many unknowns

about the waste and it is not possible to know in advance how many samples will be required, but rough estimates have been prepared based on the proposed sampling strategy.

An estimated 12% of retrieved drums will contain dangerous waste constituents, but of these, approximately 80% are expected to be detected through means other than random sampling. Therefore, only an estimated 900 will contain dangerous waste constituents detectable only through sampling. These will not occur randomly, but often will be in clusters. Based on analysis of clusters where dangerous waste constituents is documented, approximately 40% of retrieved drums will occur in lots with no dangerous waste constituents detectable through sampling, and an additional 20% in lots with only trace amounts of dangerous waste constituents that still will require only minimum sampling. The remaining 40% of lots will be subject to strategies of lot subdivision, increased sampling, or designation of the entire lot as dangerous waste. The economic analysis involved in deciding on increased sampling is very dependent on the type of process sampling used. That is, the relative economy of remote detection, if it were used, makes increased process sampling more attractive. Based on currently planned sampling methods, these estimates result in total process sampling rates of approximately 13% of all drums, leaving more stringent analysis to meet regulatory requirements on about 3% of all drums.

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MULTIMODALITY CHARACTERIZATION OF NUCLEAR WASTE DRUMS USING EMERGING TECHNIQUES FOR NONDESTRUCTIVE EXAMINATION AND ASSAY

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ABSTRACT. We are developing an x-ray imaging system that incorporates several inspection technologies for complete, nondestructive evaluation of containers of nuclear waste. In Phase I and Phase II SBIR programs for the Department of Energy (DOE), we proved the feasibility of using x-ray computed tomography (CT) and digital radiography (DR)—imaging techniques using x-rays transmitted through the object—for container inspection. Now, with further funding from DOE and working with scientists at Lawrence Livermore National Laboratory, we are designing a mobile inspection system that will use CT and DR as well as two x-ray emission imaging techniques—single photon emission computed tomography and nondestructive assay. This system will provide much more information about the contents of containers than currently used inspection methods, and will provide archiving of digital data. In this paper, we describe inspection system and present recent results from the CT and DR evaluations.

X-RAY INSPECTION OF NUCLEAR WASTE

X-ray imaging is an established method for waste container inspection. However, the technique generally used, real time radiography (RTR), has limited density discrimination and does not provide much information about the contents of dense objects such as cement-solidified drums. The RTR system couples a TV camera to a two-dimensional, light-producing x-ray detector, and thus provides a TV image that is viewed on a monitor during x-ray exposure. The dynamic range of such a system is usually from 6 to 12 bits (64 to 4096 gray levels in the image), meaning that contrast resolution in a single exposure is very limited. Also, no quantitative evaluation of the image is possible, since it is not in digital form.

Emerging technologies for nondestructive evaluation (NDE) of low level, transuranic, and mixed nuclear waste include x-ray computed tomography (CT) and digital radiography (DR). The solid-state detectors used in CT/DR imaging have enough dynamic range to provide contrast sensitivity approaching 12 to 16 bits (up to 65,536 gray levels). The higher the dynamic range, the greater the advantage in examining denser waste forms such as a grout matrix. In CT, x-ray data are collected through a thin plane of the object, using a linear detector array, while the object rotates in the x-ray beam. The data are then mathematically combined to form a cross sectional image of the irradiated plane. Figure 1 illustrates the concept of CT scanning. In DR, the object is moved past the linear detector array while projection data are collected a line at a time. The lines are then displayed as a two-dimensional projection image. Figure 2 shows the concept of DR scanning.

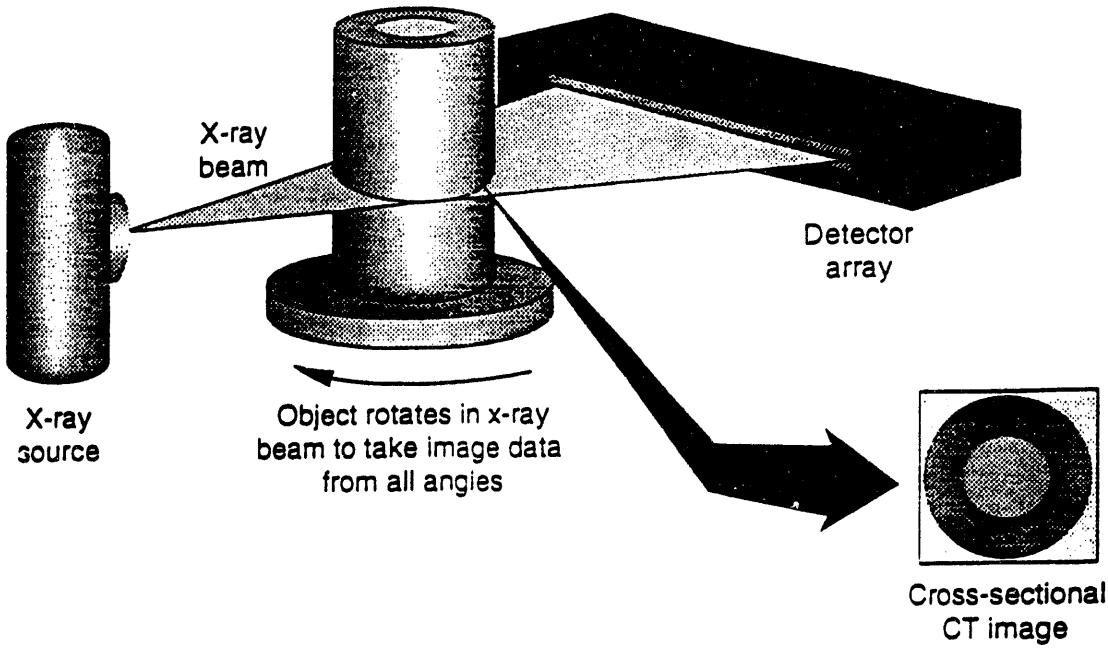

Figure 1. The drawing illustrates the concept of CT imaging.

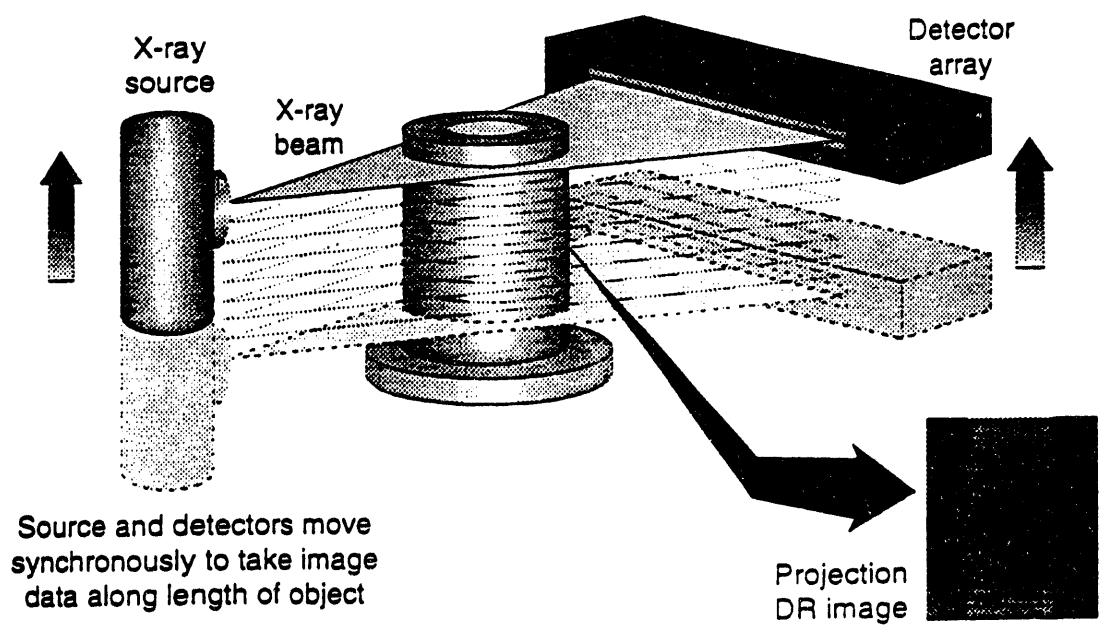

Figure 2. The drawing illustrates the concept of DR imaging.

Preliminary studies (1-3) have shown that 2 MeV transmission CT has the ability to identify and quantify free liquid volumes and heavy metals. These attributes are important in determining the safety of waste containers for transportation and permanent storage. CT can also provide three-dimensional imaging and identification of the waste form without the need for drum opening, and can measure drum wall thickness to determine the presence of corrosion and thinning before leaks occur. DR can identify dense masses and locate objects in containers, and can be used as a screening procedure to determine locations for more precise inspection using CT. Figure 3 is a 2 MeV DR image of a 55 gallon drum of simulated nuclear waste. With one x-ray exposure, DR can image high and low density materials in the same data set.

Figure 4 is a volume CT representation of a 55 gallon drum segment constructed to simulate a nuclear waste drum. The volume display consists of 30 CT slices, each 5 mm thick. Note the drum side wall showing the thicker weld seam and an area where the wall has thinned to about 0.25 mm from a normal thickness of 1.5 mm. In Fig. 5, a single slice of the volume data set in Fig 4 shows one can of spray lubricant to be empty and another to be full. The thinned drum wall adjacent to the weld seam is also indicated in this image. Figures 6 and 7 are, respectively, a volume CT representation and a single-slice CT image of a 55 gallon drum of grout, or cement. In Fig 6, numerous inserts of materials with various densities are visible. In Fig 7, a volume of water equal to 635 mL is visible as white in the image; the black is where cement has been mathematically subtracted from the image.

EMISSION IMAGING TECHNIQUES

Two emission imaging techniques will be employed for characterizing materials in water containers. The first of these is gamma emission tomography, commonly called single-photon emission computed tomography (SPECT). Rather than using an external radiation source, SPECT uses the emission of radioactive materials within the object of interest for imaging. In this case, emission from actual nuclear waste within a container will provide a three-dimensional image of the radioactive substances in the container.

The second emission technique will use high-purity germanium detectors for gamma ray spectroscopy. This technique, called nondestructive assay (NDA), can identify the emitting isotopic species and strength. Work in emission tomography and assay of nuclear waste has been undertaken at Lawrence Livermore National Laboratory using a technique called Passive Tomography (4,5,6).

MOBILE WASTE INSPECTION SYSTEM

It is feasible to combine all four of these imaging modalities into a single instrument, using common hardware, for nondestructive waste drum examination. Such an instrument can identify the shape, location, species, and strength of isotopes within a container, and can determine the safety of the drum wall and the shapes of its contents. This determination including identifying the presence of harmful free liquids and heavy metals. Potentially, nondestructive and noninvasive characterization of nuclear waste drums using a multimodality approach can offer the waste generator, storage site, and regulator a means to certify waste for safety, through quantification of critical container properties using emerging technologies.

We plan to incorporate all of these technologies into an inspection system that will be built in a single mobile trailer; all modalities will share the same mechanical drum manipulator, image processing computer, and display . Figure 8 shows a mobile trailer concept for imaging drums with a multimodality NDE/NDA approach. Drums are loaded or unloaded with a forklift truck and or conveyor system. The trailer is self-sufficient, with its own electrical generator and HVAC equipment. A 2 MeV radiation shielded scanner room, equipment room, and control room are shown.

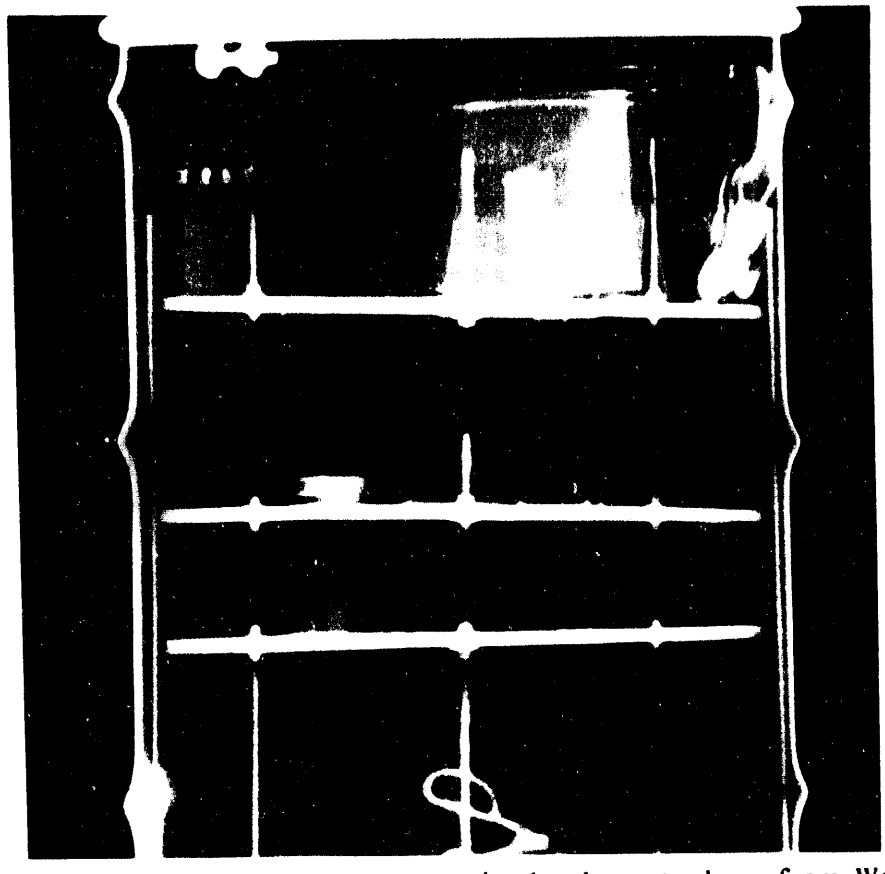

Figure 3. This DR image of a phantom, or simulated, waste drum from Westinghouse Hanford was taken at 2 MeV. Identifiable features include an aluminum step wedge in the top layer, partially filled and empty spray cans in the second layer, vials of different materials in the third layer, and a scissors and paints cans in the fourth layer.

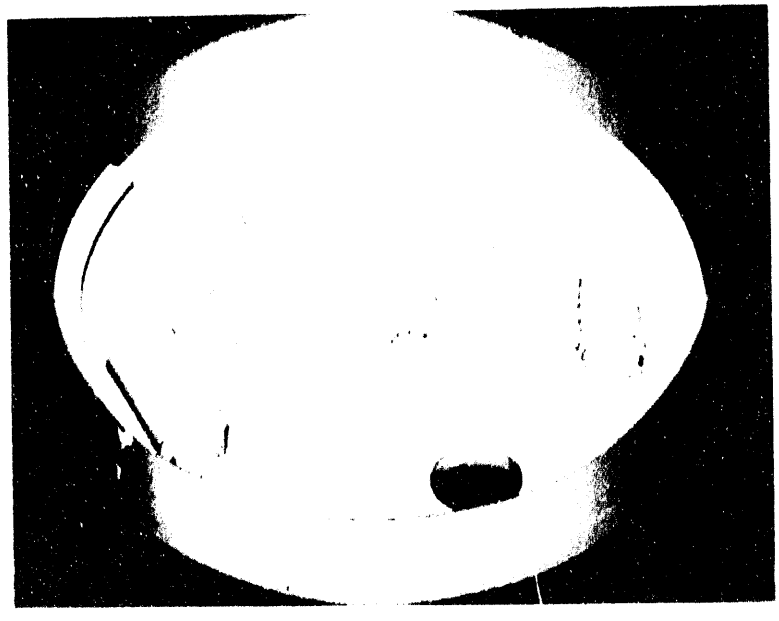

Figure 4. This three-dimensional data set of a phantom drum section consists of 30 adjacent CT slices. Two WD40 spray cans are resting on a layer of cement. At the bottom left (at about the eight o'clock position), the weld seam is visible as a white line in the drum, with a thinned section of the drum wall visible next to it.

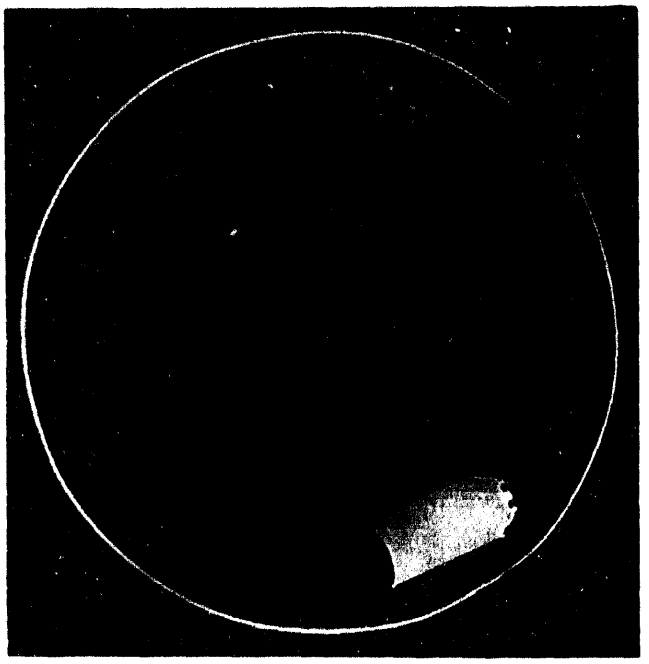

Figure 5. This CT image shows the assorted items in the top section of the phantom seen in Figure 4. Note the thin section of the steel drum wall, at the five o'clock position near the line cursor. The swirling shapes are blue jeans, which were not visible in Figure 4 because of the data window setting.

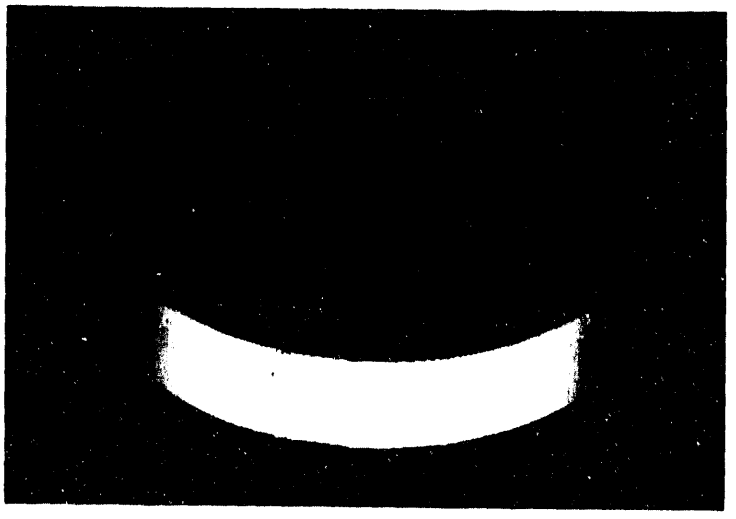

Figure 6. This is the same data set shown in Figure 4, but it has been rotated to show the bottom of the cement layer.

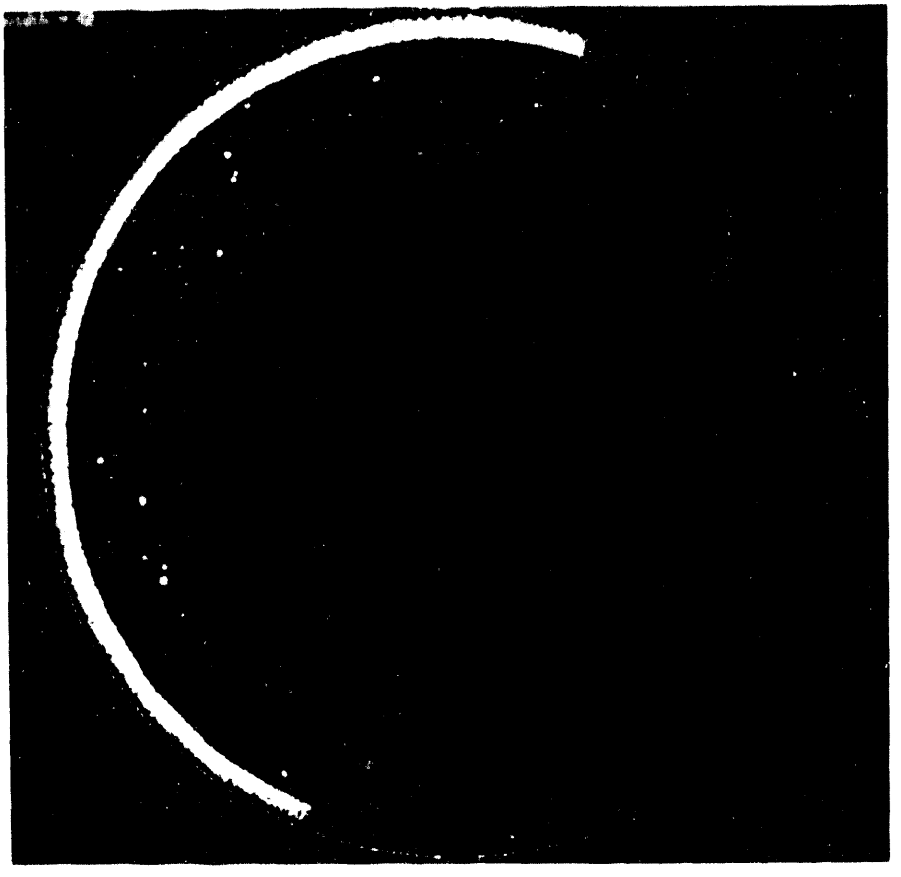

Figure 7. This CT image of a phantom drum shows a water-saturated cement layer with a water rim around half the circumference. The smallest pores visible here are only fractions of cubic millimeters in size. The calculated volume of water in this image is 635 ml.

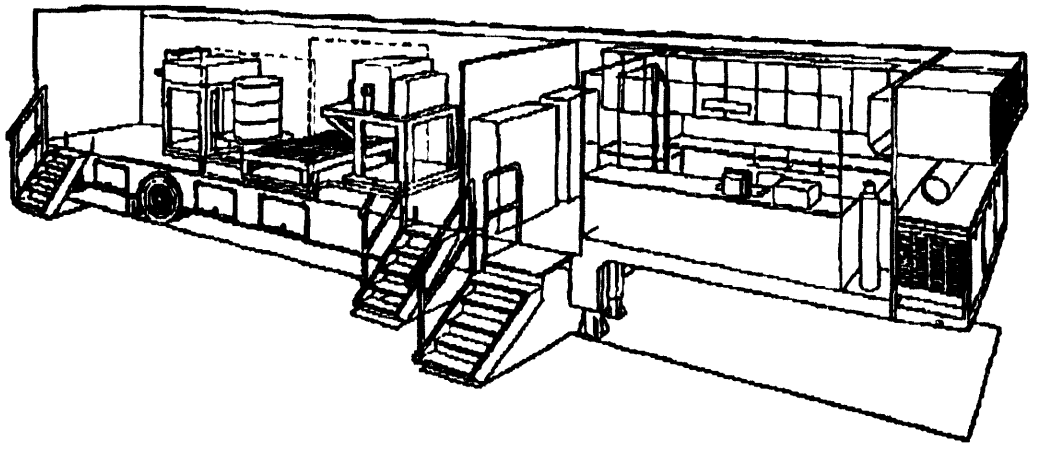

Figure 8. The drawing illustrates the mobile waste inspection system

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LONG-RANGE ALPHA DETECTION APPLIED TO MIXED-WASTE MONITORING

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ABSTRACT. Much of the waste that is classified as "mixed" is only assumed to be radioactive. Waste materials (toxic or other) taken from a contaminated area are generally assumed to be contaminated and are disposed of as radioactive or (if the waste material is toxic) mixed waste. The quantities of both radioactive and mixed waste could be greatly reduced if the waste could be effectively monitored prior to disposal. Traditional detection systems excel at locating beta and gamma contamination on waste materials; however the short range of alpha particles in air severely hampers the efficient detection of alpha contamination on waste material. To compound this problem, many transuranic contaminants, such as ^{239}Pu, emit primarily alpha radiation and are difficult to detect using conventional technology. The long-range alpha detection (LRAD) system detects the ions that are generated by alpha particles passing through the air, rather than the alpha particles themselves. Thus, the LRAD response is limited only by the range of ions in air (many meters) as opposed to the range of the parent alpha particles (several centimeters). In addition, the LRAD can detect alpha contamination inside any object or matrix through which air can flow freely (such as loosely packed solid waste). The LRAD detectors are window-less, rugged, and have been successfully operated in field conditions. These characteristics make the LRAD an ideal detector for use on mixed, solid, or liquid waste streams, with applications in environmental restoration, solid- and liquid- waste monitoring, arms control, and air-quality monitoring.

INTRODUCTION

Traditional alpha contamination monitoring relies upon direct detection of alpha particles as illustrated in Fig. 1. Alpha particles are relatively massive and slow moving, giving all of their energy to ion pairs within a few centimeters. To be detected, alpha particles must pass through air and still have enough energy remaining to penetrate a traditional detector surface. As a result, direct detection of alpha particles has at least four limitations.

(1) Traditional alpha detectors are only sensitive to contamination located directly under the detector probe. Therefore, any contamination that is on a convoluted surface becomes difficult or impossible to monitor satisfactorily.

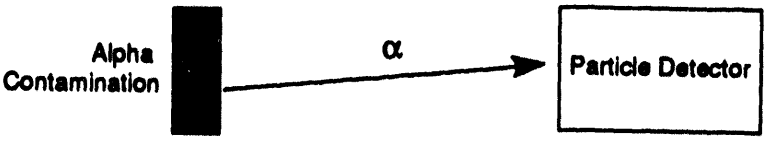

Figure 1. Traditional alpha contamination monitoring relies upon direct detection of alpha particles.

(2) Increasingly strict monitoring thresholds have surpassed the capabilities of traditional monitors. Regulations dictate reliable radiation monitoring of several hundred disintegrations per minute (dpm), whereas traditional monitors can only reliably measure contamination of 1000 dpm.

(3) Because traditional monitors can only monitor contamination located directly under the hand-held probe, accurate scanning of large surface areas that are uniformly contaminated becomes very difficult.

(4) Alpha scanning must presently be done by hand, and the ability to do a good job varies from worker to worker, creating variables that are impossible to standardize (1).

Intrinsic limitations caused by traditional alpha detection technology have created a situation where traditional alpha detectors cannot keep pace with current regulatory requirements. Because of these limitations, much of the waste is categorically termed as radioactively contaminated, creating a voluminous mixed-waste situation.

THE PROBLEM OF ALPHA CONTAMINATION IN MIXED WASTE

Transuranic isotope production is relatively easy. Unfortunately the detection of this type of radioactive decay has proven to be difficult. Because of the difficulty detecting alpha contamination, waste-management personnel and health specialists who work at production or clean-up sites have to assume that much of the disposal contains radionuclides alone or mixed waste.

Mixed waste is harder and more expensive to handle than either radioactive or toxic waste alone. If it were possible to identify alpha contamination with greater sensitivity and higher confidence levels than present technology allows, the cost of storing or disposing of mixed waste would be greatly reduced and managing it at many of these sites would be easier.

The long-range alpha detector (LRAD) offers a solution to many of the problems described above. The LRAD monitor is sensitive to low levels of alpha contamination; it is automated, eliminating human error; it can "see" contamination in convoluted environments; and it can monitor large areas quickly and accurately.

LRAD OPERATION

The (LRAD) depicted in Fig. 2 detects ions created by the ionizing alpha particle. As an alpha particle loses energy in air, it creates many ion pairs; these ions have long ranges compared to the alpha particle and can be transported many meters in an air flow. An ion detector located in the air current can detect and quantitatively measure the number of ions as a function of current.

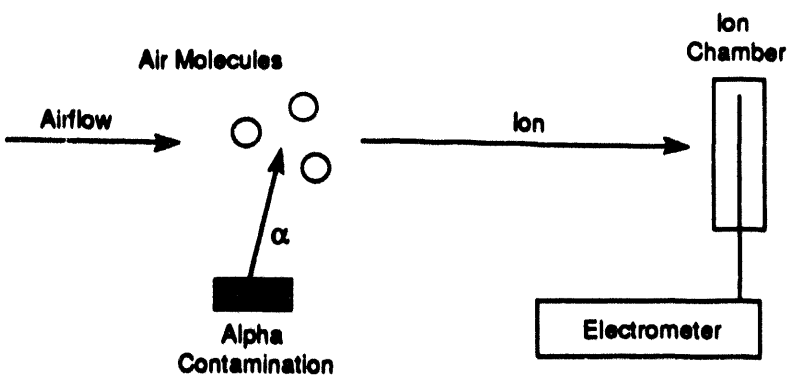

Figure 2. The LRAD detects ions created by the ionizing alpha particle.

In ambient air, an alpha particle imparts about 35 eV per ion pair created, thus a 5-MeV alpha particle will produce approximately 150,000 ion pairs. An air current or electric field transports the charged particles into an ion detector. The signal response is proportional to the number of ions; hence, as contamination activity increases, the signal response increases linearly, as illustrated in Figs. 3 and 4 (1). The LRAD can detect contamination on the order of 100 dpm, compared with traditional monitors, which can detect contamination of 1000 dpm only under ideal conditions.

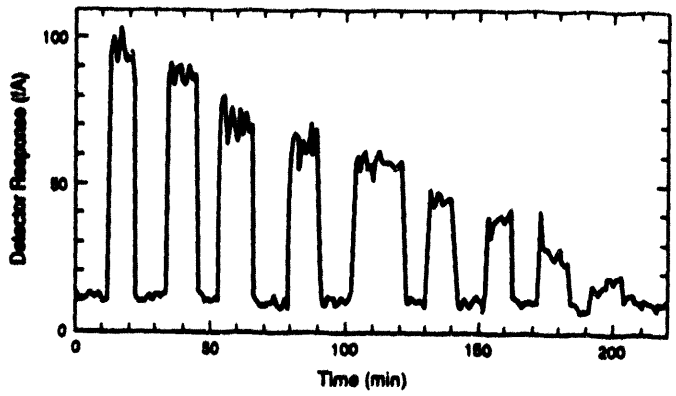

Figure 3. LRAD response (from left to right) to 9 ^{234}Pu sources, ranging from 1100 to 100 dpm. All 9 source strengths can be read from Fig. 4.

DETECTOR CONSTRUCTION

The LRAD system has two primary designs: airflow and fan-less. The airflow model moves the ions via a fan-generated airflow; the fan-less model uses an electric field to draw the ions onto a signal plane.

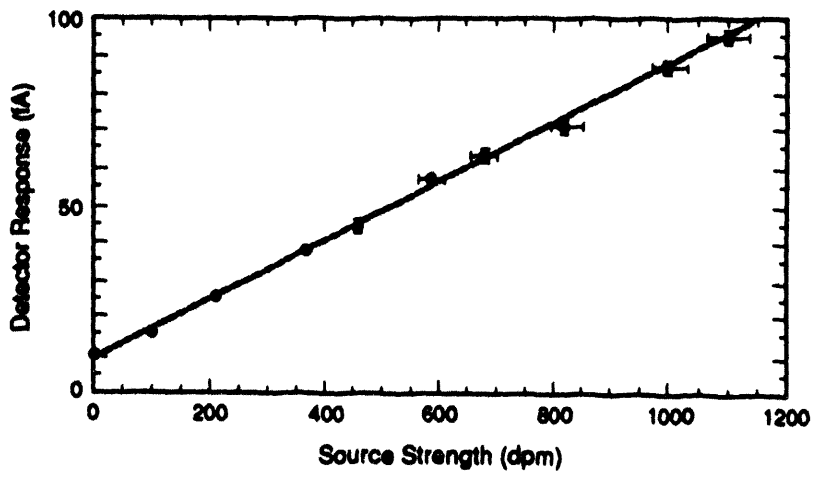

Figure 4. Detector responses (source and background) of Fig. 3 analyzed and plotted as a function of source strength.

Airflow Model

In the airflow design LRAD, ionized particles are drawn into a region between two grids, where a battery applies a voltage to the grids, creating an electric field. The electric field attracts one of the charged ions (positive or negative) to the high-voltage (HV) grid while pushing the other ion onto the sense grid, as illustrated in Fig. 5 (1).

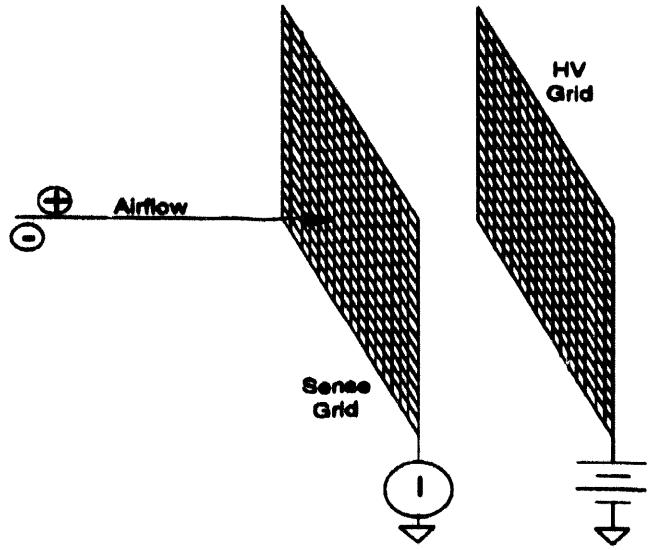

Figure 5. Construction details of a two-grid ion detector.

An airflow created by fans draws the ions into the grid area. The HV grid can be sensitive to either ion, positive or negative; Fig. 6 shows that both polarities have equal sensitivity to the detection grid (2). Each ion that interacts with the grid creates a small increment of current; thus, the more ions, the larger the current. Currents flowing through the sense grid pass through an electrometer and are sent to a data acquisition system.

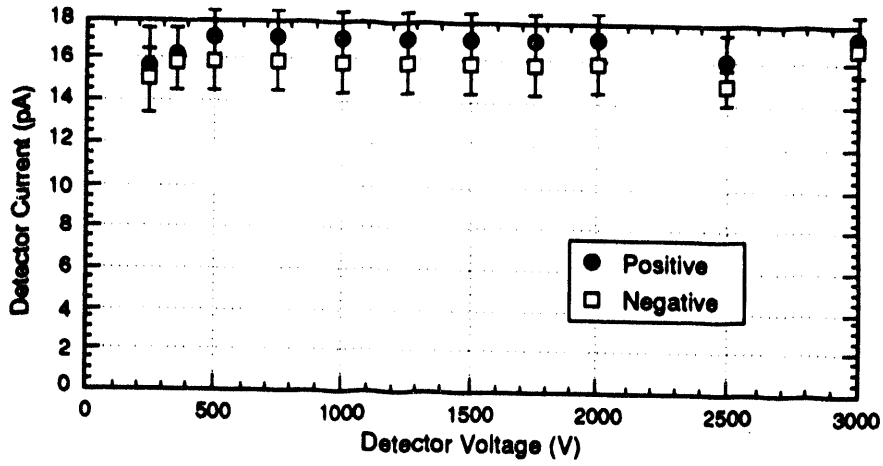

Figure 6. Results of LRAD operation with positive or negative HV applied to the grid.

Fan-Less Model

The fan-less LRAD is a five-sided enclosure, a cross section of which is shown in Fig. 7. The open side of the enclosure is placed over the contamination, essentially using the contaminated plane as the sixth side of the box. A signal plane is located at the top of the LRAD. Applying a voltage charge to the sense plane creates an electric field that attracts the charged ion.

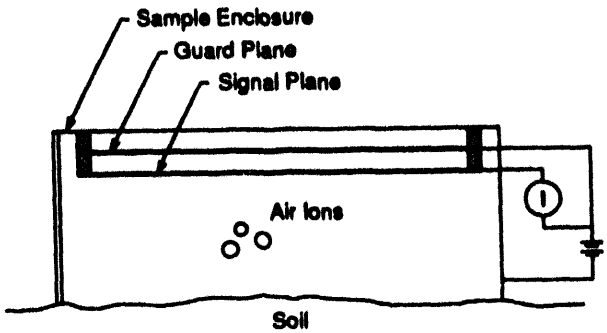

Figure 7. The fan-less LRAD used in surface monitors. No airflow is required in this LRAD, since the ions are electrostatically attracted to the signal plane, where the ion current is read out by the electrometer.

APPLICATIONS FOR LRAD MONITORING

The LRAD technology has many applications for mixed-waste management. The two basic designs, airflow and fan-less, can be adapted to meet the specific needs of the monitoring applications. Some of these applications and their specialized monitors, which are representative of just a few of the potential uses of LRAD to mixed-waste management, are discussed below.

Applications for Tool and Equipment (Object) Monitoring

Often when old or disabled tools and equipment are removed from nuclear facilities it must be assumed that the object has been contaminated with alpha-emitting uranium or transuranic isotopes. When the item is too large or convoluted to monitor using conventional methods, an LRAD object monitor could quickly and effectively monitor such items.

The tool monitor (Fig. 8) is a box constructed of stainless steel or aluminum. From right to left, the intake manifold is equipped with an electrostatic filter designed to screen airborne particulate and ambient ions that could interfere with contamination detection. The object chamber is an enclosed area comprising an access door; a screen stand that is for objects with potential 4-pi contamination; and an ion chamber that is located in front of the fan manifold. Alpha-created ions are drawn into the ion chamber, then the current is interpreted by an electrometer.

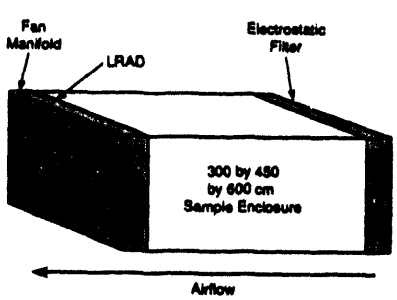

Figure 8. Simplified drawing of a large LRAD object-monitoring system.

In LRAD tests for source response of several different tool configurations, using a ^{239}Pu source as the "contamination," the source was placed in the center of five objects (Fig. 9) that could be construed as typically contaminated objects. For each object, we found the minimum source response (in disintegrations per minute) that could be reliably detected. Figure 10 shows the minimum activity that was confidently detected with 99.9% certainty using LRAD (1).

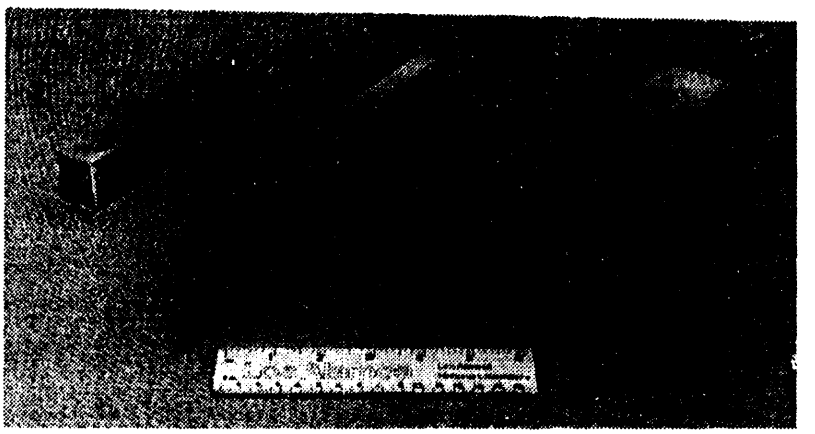

Figure 9. Photograph of five typical solid-waste objects. Starting in the upper left corner and moving clockwise, they are a piece of pipe, an aluminum channel, an aluminum "pig" with a 1/2-in. hole drilled through it, a small Pomona® box, and a hammer head.

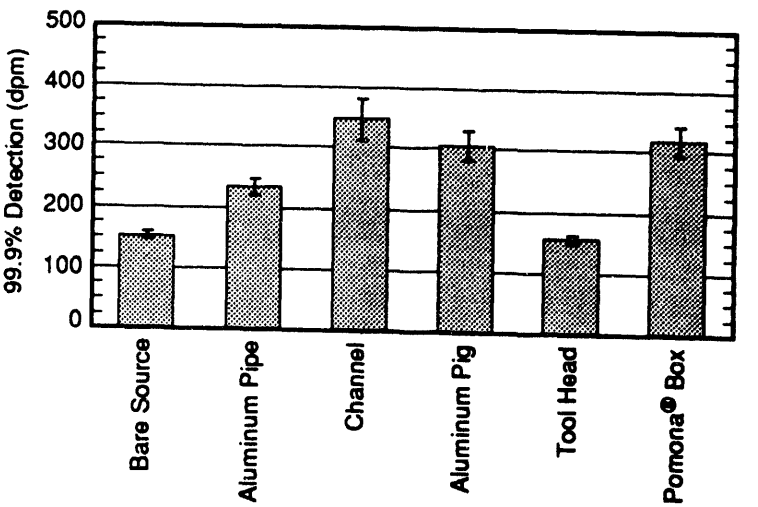

Figure 10. Minimum detectable source responses (with 99.9% certainty) in each of the five mockups illustrated in Fig. 9, as well as the minimum detectable bare source.

The graph in Fig. 10 shows that the tool head has the same minimum activity response as the minimum bare source, which is expected because the tool head is in the open, unencumbered by any obstructions. The channel, with the source in the interior of the channel tunnel, proved to be the least responsive tool configuration, requiring a source of 350 dpm as a confident lower detection limit. If that channel were monitored with traditional methods, it would still be impossible to detect alpha contamination, even as the activity increases, because of the placement of the contamination. This data conservatively predicts reliable contamination detection of 300 - 500 dpm, regardless of the shape of the waste.

Already built or under construction are object monitors in several size configurations, including small, medium, and portable field units. Test results show that the object monitor's chamber volume has no bearing upon contamination detectability; as the volume changes, the source calibration changes. Once a monitor has been calibrated, it is ready to use.

Applications for Solid-Waste Monitoring

The solid waste LRAD monitor has three potential uses:

(1) Solid-waste-stream monitoring: A conveyor belt moves waste in a solid stream through an LRAD. At predetermined radiation activity levels, the machine sounds an alarm, stopping the conveyor belt and warning the operator of contamination. Contaminated matter can then be removed from the waste stream and monitored more thoroughly in an object monitor. This method would substantially reduce the volume of mixed and radioactive waste.

A tungsten block with alpha contamination is representative of a typical piece of waste that would trigger the LRAD solid-waste-stream monitor. Putting the tungsten block into an object monitor and comparing it to a 200-dpm source and a clean block resulted in the data graphed in Fig. 11, which shows that the LRAD responded to the contaminated block within one minute (1). Subsequent monitoring with a traditional hand-held monitor took several hours to detect the contamination.

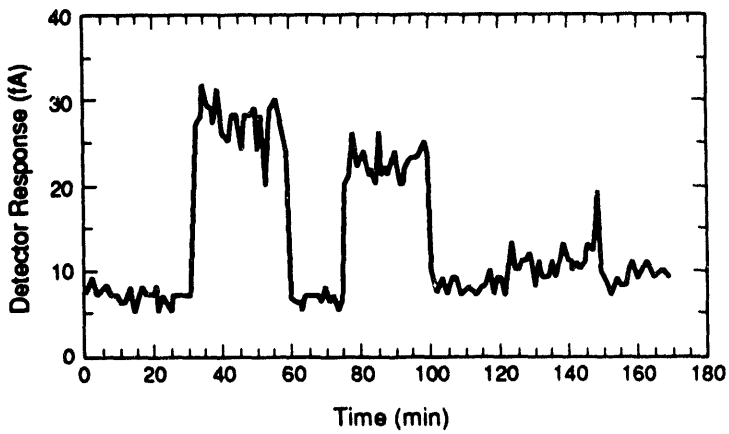

Figure 11. Response of the LRAD system to a contaminated block (35 - 60 min); a 200-dpm ^{239}Pu source (75 - 100 min); and a relatively uncontaminated block (125 - 150 min). Removing the block caused the spike at 150 min. All regions between the measurements represent detector background.

(2) Bulk monitoring: The LRAD could be used as a bulk monitor when it is suspected that hazardous waste has become alpha contaminated. Here, loosely packed waste would be put into a dumpster, where in-flow and out-flow fans would provide a robust air flow to transport any ions created by contamination. These ions would then be deposited onto the detection grid and interpreted by the data acquisition system.

(3) Point-of-entry monitoring system: A discrete separation system designed to discriminate against radioactive waste at the point of disposal would reduce mixed waste. All waste would be put into an LRAD hopper for monitoring, where an alarm would signal alpha-contaminated waste. Uncontaminated waste could then be dealt with accordingly.

Applications for Liquid-Waste Monitoring

We have developed four potential LRAD applications for monitoring liquid waste using a system that depends upon the situation, suspected contamination levels, and viscosity of the waste:

(1) Liquid-waste monitor: A liquid waste stream flowing through a fan-less LRAD will monitor the alpha constituents. The stream needs to be wide and shallow, moving with minimal velocity. These conditions are necessary to provide a large surface area for alpha particles to escape from the waste.

A source is placed in a tray of water, with the contaminated surface of the source even with the plane of the water. The graph in Fig. 12 shows that the water did not impede the ability of LRAD to detect the source.

(2) Dry/liquid waste monitor: Percolating air through a volume of liquid waste in a crock-pot-style container will drag any ionization to the surface to be monitored by a portable LRAD unit attached to the lid.

(3) Monitor for low-viscous liquids: A representative sample of the waste is atomized by a spray nozzle into a small LRAD chamber, where contaminated droplets would ionize the air. The ions would then be collected on the detection grid.

(4) Evaporation monitor: Another technique involves evaporating the waste and monitoring the resulting residue in an object monitor. This approach requires pouring very shallow puddles of the liquid waste into bins on a conveyer belt. Each bin would first be subjected to intense heat lamps to evaporate the moisture, then monitored in an object monitor. This method would also reduce the volume of liquid or mixed waste.

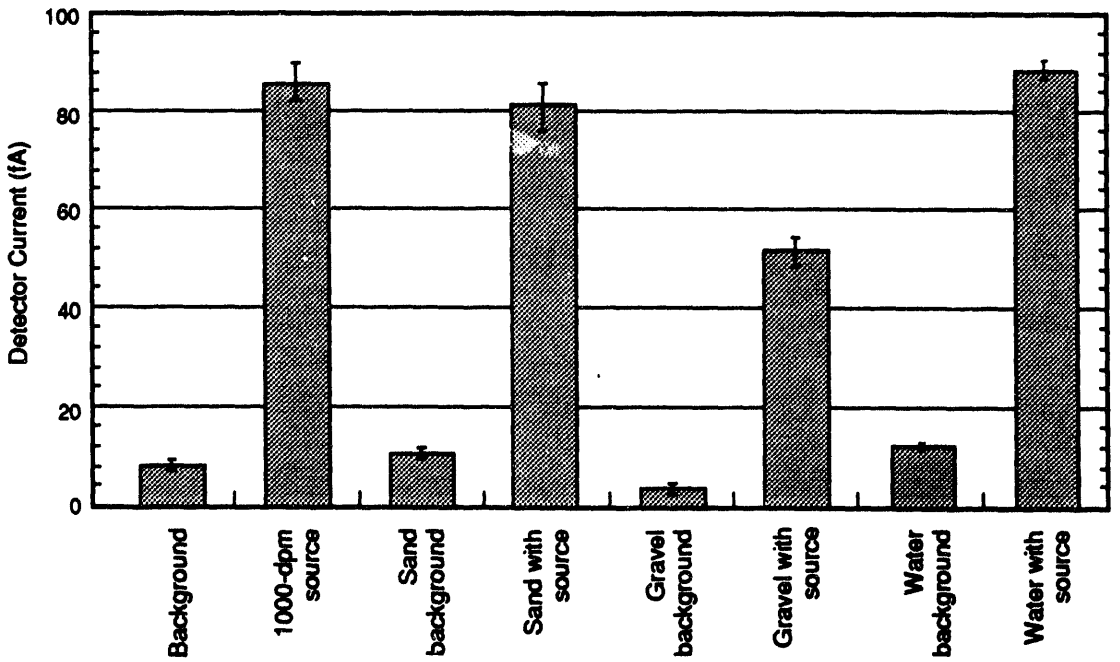

Figure 12. Effects of sand, gravel, and water on source and background measurements in an LRAD monitor.

Applications for Decontamination and Decommissioning Monitoring

As nuclear facilities around the world are decommissioned, a potential mixed-waste issue is emerging. Many buildings exist where production has been performed for 40 or more years, and documentation of old spills and accidents is non-existent or uninformative. The LRAD could be a useful aid in reducing the amount of waste that must be handled in accordance with strict regulations, thereby saving money and mixed-waste disposal space. The following scenarios demonstrate the LRAD's potential usefulness:

- A typical method for "cleaning" an alpha spill is to paint over it. The LRAD could be used to monitor tiling, sheet rock, and plaster that is removed from buildings to separate the radioactive waste from everything else.
- The plumbing from many of these old buildings is made of lead, a hazardous waste; however, it is impossible to easily monitor the interior of these pipes for radiation contamination using conventional methods. An adaptation of LRAD technology, shown in Fig. 13, provides an easy, inexpensive procedure for monitoring the interior of these pipes. By attaching a filter and fan to one end of a pipe section and an ion grid/fan arrangement to the other end of the pipe, the interior of the pipe becomes the actual ion chamber, and any interior contamination would register on the grid. To monitor the exterior of the pipe, place the pipe section into an object monitor (3).

Applications for Barrel Monitoring

In many parts of the country, mixed waste is stockpiled in barrels awaiting the construction of suitable storage facilities. Maintaining the integrity of the barrel becomes an important issue, since leaks are often not discovered until they have become a spill. In this case, the LRAD could be useful in monitoring temporary storage sites. On a periodic schedule, barrels could be monitored in a large barrel monitor, similar to a large version of the tool monitor. Any small cracks or fissures in the barrel would allow radioactive contamination to escape. LRAD would then be able to detect even minute amounts of alpha leakage.

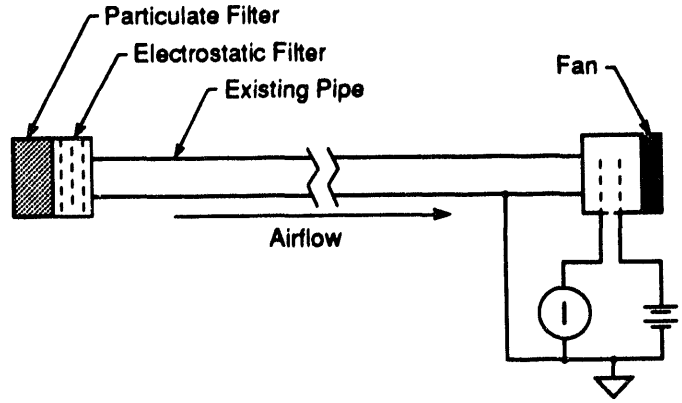

Figure 13. Schematic of a small airflow LRAD in a pipe monitor configuration. Filtered ambient air is drawn through the potentially contaminated pipe by the fan. The contamination-produced ions are detected on the first grid, and the current created by the ions is read out by an electrometer.

CONCLUSION

The trend toward tighter regulations set down by DOE, EPA, NRC, and state agencies has created a situation in which waste professionals are asked to protect the public against radiation levels that are not detectable using current technologies. The LRAD technology provides an answer to some of the detection problems mixed-waste specialists will be asked to address in the coming years. Our results indicate that LRAD can be useful in many types of alpha monitoring that are currently difficult to perform.

ACKNOWLEDGEMENT - This work was sponsored by the U.S. Department of Energy, managed by the Los Alamos National Laboratory (Contract W-7405-ENG-36).

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2. MacArthur, D.W. and Allander, K.S., Long-range alpha detectors, LA-12073-MS, Los Alamos National Laboratory, Los Alamos, NM (July 1991).
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UNSTEADY-STATE VOC TRANSPORT IN VENTED WASTE DRUMS

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ABSTRACT. A model of unsteady-state volatile organic compound (VOC) transport in a vented waste drum has been developed. Model predictions of the VOC concentration in the innermost layer of confinement and the drum headspace are compared to measurements in lab-scale simulated waste drums.

INTRODUCTION

Knowledge of volatile organic compound (VOC) releases from vented waste drums as well as VOC concentrations within the waste drum is becoming more important with increasing environmental and safety regulations and guidelines. These regulatory demands are the motivation for a better understanding of unsteady-state VOC transport from vented waste drums. An accurate model capable of describing VOC transport out of a vented waste drum can be a useful tool to estimate maximum venting times, expected VOC releases, and estimated VOC concentrations within layers of confinement in a waste drum.

VOC TRANSPORT MODEL

A VOC transport model has been developed to estimate the transient VOC concentration throughout a simulated waste drum. The model consists of a series of material balance equations describing unsteady-state VOC transport between each layer of confinement. A simulated waste drum consists of a scaled-down metal drum containing a rigid polymer polyethylene drum liner that holds a large polyethylene bag with four smaller polyethylene bags initially filled with a VOC-air mixture. Waste drums are vented by placing a carbon-composite filter through the drum lid and a 0.0095-m diameter hole punctured in the drum liner lid directly below the filter. The small bags filled with the VOC-air mixture are the first and innermost layer. The large bag, drum liner and drum are the second, third, and fourth layers of confinement, respectively.

The important mechanisms of VOC transport within a waste drum are VOC permeation and diffusion to an adjacent void volume and solubilization into a polymer. The rate of VOC permeation across a polymer film is defined by

$$Q_{P,i} = \mathcal{P} A_{P,i} \frac{\Delta p}{\Delta x_{P,i}} \qquad (1)$$

where

$Q_{P,i}$	=	rate of VOC permeation from i^{th} void volume, mol s^{-1}
$\mathcal{P}$	=	VOC permeability coefficient, mol m^{-1} Pa^{-1} s^{-1}
$A_{P,i}$	=	surface area across which VOC permeates from i^{th} void volume, m^2
Δp	=	VOC partial pressure difference across polymer boundary, Pa
$\Delta x_{P,i}$	=	thickness of polymer boundary surrounding i^{th} void volume, m.

The rate of VOC diffusion in air is defined by

$$Q_{D,i} = DA_{D,i} \frac{\Delta c}{\Delta x_{D,i}} \tag{2}$$

where

$Q_{D,i}$	=	rate of VOC diffusion from i^{th} void volume, mol s^{-1}
D	=	VOC diffusivity in air, m^2 s^{-1}
$A_{D,i}$	=	cross-sectional area of diffusional path across i^{th} void volume, m^2
Δc	=	VOC concentration difference across opening, mol m^{-3}
$\Delta x_{D,i}$	=	diffusional path length between void volumes, m.

Most VOCs are soluble in polymers and will accumulate within a polymer until an equilibrium concentration is reached. The rate of accumulation is defined as

$$P\frac{ds_i}{dt} = \eta P[s_{\infty,i} - s_i] \tag{3}$$

where

s_i	=	average VOC solubility in i^{th} polymer volume, mol m^{-3} Pa^{-1}
$s_{\infty,i}$	=	VOC equilibrium solubility in i^{th} polymer volume, mol m^{-3} Pa^{-1}
η	=	transfer coefficient, s^{-1}
P	=	absolute pressure, Pa.

The total rate of VOC transport from each small polymer bag is defined by summing the contribution of each transport mechanism defined by equations (1)-(3)

$$\left[\frac{d(Vc)}{dt}\right]_{1,j} = \left[\frac{\Phi A_P}{\Delta x_P}\right]_{1,j} \Delta p + \left[\frac{DA_D}{\Delta x_D}\right]_{1,j} \Delta c - \left[f V_p P \frac{ds}{dt}\right]_{1,j} \tag{4}$$

where

$V_{1,j}$	=	void volume within j^{th} small bag, m^3
$c_{1,j}$	=	VOC concentration in $V_{1,j}$, mol m^{-3}
dt	=	differential time interval, s
Δp	=	$p_2 - p_{1,j}$, Pa
p_i	=	VOC partial pressure in V_i, Pa
Δc	=	$c_2 - c_{1,j}$, mol m^{-3}
c_i	=	VOC concentration in V_i, mol m^{-3}
$f_{1,j}$	=	$c_{1,j} V_{1,j}/[c_{1,j} V_{1,j} + c_2 V_2]$
$V_{p,1,j}$	=	polymer volume of j^{th} small bag, m^3.

In defining the coefficient f, it was assumed that the number of moles sorbed on a polymer film from a void volume was proportional to the total number of moles available in all void volumes adjacent to the film. In order to calculate the change of VOC concentration as a function of time, p_i is defined in terms of c_i

$$p_i = c_i R T_i \tag{5}$$

where

R	=	gas constant = 8.314 m^3 Pa mol^{-1} K^{-1}
T_i	=	temperature in i^{th} void volume, K.

Substitution of eqn (5) into eqn (4) yields

$$V_{1,j}\frac{dc_{1,j}}{dt} = (\alpha + \beta)_{1,j}[c_2 - c_{1,j}] - \gamma_{1,j}\frac{ds_{1,j}}{dt} \tag{6}$$

where

$\alpha_{1,j}$ = $RT_1(\mathcal{P}A_p/\Delta x_p)_{1,j}$
$\beta_{1,j}$ = $(DA_D/\Delta x_D)_{1,j}$
$\gamma_{1,j}$ = $(fV_pP)_{1,j}$.

The VOCs exiting the small bags enter the void space within the large bag. The equation for the VOC molar rate of change in the large bag is defined as

$$V_2\frac{dc_2}{dt} = \left[\sum_{j=1}^{4} -(\alpha+\beta)_{1,j}[c_2 - c_{1,j}]\right] + (\alpha+\beta)_2[c_3 - c_2] - g(s_1, s_2) \tag{7}$$

where, in general

$$g(s_k, s_m) = (1-\gamma_k)\frac{ds_k}{dt} + \gamma_m\frac{ds_m}{dt} \quad . \tag{8}$$

In the liner and drum lids there are relatively large openings through which VOCs exit by diffusion and convective flow resulting from changes in temperature. In the case of increasing temperature, the VOC molar rate of change in the liner headspace is defined as

$$V_3\frac{dc_3}{dt} = \left[\sum_{i=2}^{3}(-1)^{3-i}(\alpha+\beta)_i[c_{i+1} - c_i]\right] - g(s_2, s_3) - \frac{V_3c_3}{T_3}\frac{dT_3}{dt} \quad , \tag{9}$$

and in the drum headspace the VOC molar rate of change is defined as

$$V_4\frac{dc_4}{dt} = -(\alpha+\beta)_3[c_4 - c_3] - D^* c_4\frac{T_4}{T_o} - g(s_3, s_4) + V_4c_4\left[\frac{T_4}{T_3^2}\frac{dT_3}{dt} + \frac{1}{T_4}\frac{dT_4}{dt}\right] \tag{10}$$

where

D^* = VOC-filter diffusion characteristic, $m^3\ s^{-1}$
T_o = gas temperature during filling of small bags, K.

In the case of decreasing temperature, the VOC molar rate of change in the liner headspace is defined as

$$V_3\frac{dc_3}{dt} = \left[\sum_{i=2}^{3}(-1)^{3-i}(\alpha+\beta)_i[c_{i+1} - c_i]\right] - g(s_2, s_3) - \frac{V_3c_4}{T_3}\frac{dT_3}{dt} \quad , \tag{11}$$

and in the drum headspace is defined as

$$V_4 \frac{dc_4}{dt} = -(\alpha + \beta)_3[c_4 - c_3] - D^* c_4 \frac{T_4}{T_o} - g(s_3, s_4) + \frac{V_4 c_4}{T_3} \frac{dT_3}{dt} \quad . \tag{12}$$

The temperature dependence of VOC permeability was estimated. The transmission rate of a number of organic liquids through low-density polyethylene at different temperatures has been reported (1,2). A semi-empirical equation has been used to estimate the transmission rate for VOCs in polyethylene and related polymers (1):

$$\log_{10} Q = K - c\pi \tag{13}$$

where

Q	=	VOC transmission rate
π	=	function of VOC molecular structure.

For low-density polyethylene[1]

$$K = 16.55 - \frac{3700}{T} \quad . \tag{14}$$

The transmission rate is often used to estimate VOC permeability when the saturated vapor pressure of the permeant at a specified temperature is applied across a film (2). Thus,

$$\mathcal{P} \propto \frac{Q}{P_{vap}} \tag{15}$$

where P_{vap} is the saturated vapor pressure at temperature T. Temperature dependence of the VOC vapor pressure is estimated using the Antoine equation (3).

$$\log_{10} P_{vap} = A - \frac{B}{C + T} \tag{16}$$

where A, B, and C are equation constants. The effect of temperature on VOC vapor permeability in low-density polyethylene is estimated by combining Equations (13)-(16):

$$\log_{10} \left[\frac{\mathcal{P}(T_1)}{\mathcal{P}(T_2)}\right] = B \left[\frac{1}{C + T_1} - \frac{1}{C + T_2}\right] - 3700 \left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad . \tag{17}$$

The diffusivities of each VOC in air were identified in the literature (4) at a specific temperature and pressure or estimated by an equation developed from a combination of kinetic theory and corresponding-states arguments (5):

$$D_{AB} = 5.888 \times 10^{-10} \frac{T^{1.823}}{P} \left[p_{cA}\, p_{cB}\right]^{1/3} \left[T_{cA}\, T_{cB}\right]^{-0.495} \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2} \tag{18}$$

where

D_{AB}	=	mass diffusivity for VOC(A)-air(B) system, $m^2\ s^{-1}$
p_{ci}	=	critical pressure of species i, Pa
T_{ci}	=	critical temperature of species i, K
M_i	=	molecular weight of species i.

MODEL ASSUMPTIONS

The following assumptions were made in deriving model equations:

- All void volumes are well-mixed and the VOC concentration is identical throughout.
- The diffusion pathway length between two void volumes is the polymer boundary thickness and the mean hole diameter.
- The temperature in the small and large bags is the same as that in the drum headpsace.
- Pressure differential across puncture hole in the liner lid and drum filter is negligible.
- The VOC concentration outside the drum is 0.0 mol m^{-3}.
- VOC permeability is independent of VOC concentration in the gas phase.
- All surface areas, void volumes, and diffusion path lengths specified for a given system remain constant during the entire test period.

MODEL PARAMETERS

The permeability of each of five VOCs in a VOC-air mixture across the polyethylene bag were measured using a mixed-gas chromatographic detection method and are listed in Table 1.

Table 1. Parameter values used in model calculations.

VOC (Approximate feed concentration)	Permeability[a] mol $m^{-1}Pa^{-1}s^{-1} \times 10^{14}$	Gas solubility[a] mol $m^{-3}\ Pa^{-1} \times 10^{2}$	Transfer coefficient[b], s^{-1}
Methylene chloride (1000 µL/L)	69.7	5.9	8×10^{-7}
Freon-113 (1000 µL/L)	621	4.1	4×10^{-6}
1,1,1-trichloroethane (1000 µL/L)	351	4.3	4×10^{-6}
Carbon tetrachloride (300 µL/L)	410	6.4[b]	8×10^{-6}
Trichloroethylene (300 µL/L)	791	3.3	2×10^{-6}

a. Measured across polyethylene bags used in experiments at 25°C.
b. Estimated using lab-scale VOC transport experimental data.

The VOC-filter diffusion characteristic is a system parameter that lumps together the VOC-air diffusivity, cross-sectional area of the filter, and diffusional length. The VOC-filter characteristic across the carbon-composite filter used in these experiments was estimated based on the hydrogen (H_2)-filter diffusion characteristic measured across the same filter type and ratio of VOC-to-H_2 diffusivities in air

$$D^{\bullet}_{VOC} = \left[\frac{D_{voc}}{D_{H_2}}\right] D^{\bullet}_{H_2} \qquad (19)$$

The H_2-filter diffusion characteristic across the type of carbon-composite filter used in these experiments is 0.13 $m^3\ s^{-1}$.

Many model parameters were measured directly or estimated from available process information. All bags had a wall thickness of 1×10^{-4} m. Each small bag had an approximate internal volume of 0.004 m^3. The internal volume of the large bag was estimated to be 0.05 m^3. Large bag void volume was the difference between the total estimated internal volume of the large bag and the total volume of the small bags.

Other parameters, such as the transfer coefficient η in equation (3), were estimated using the VOC transport model and lab-scale waste drum data. Model parameters determined in this fashion were used in all other model calculations. Gas solubility in the polyethylene bag was calculated from using pressure-change permeability method. Permeability experiments to determine the gas solubility in the drum liner could not be performed because the drum liner wall thickness was too great. Gas solubility in the polyethylene drum liner was estimated from these values. Gas solubility was assumed to vary linearly with gas-phase VOC concentration as described by Henry's law (6). In the case of carbon tetrachloride, an approximation of the VOC solubility in polyethylene was estimated using lab-scale results and the VOC transport model. The gas solubilities used in the model are listed in Table 1. The transfer coefficient in eqn (3) defines the rate of VOC uptake in a polymer film. The values for each VOC were estimated using experimental data and are summarized in Table 1.

Initial VOC concentration in the small bags was assumed to be equal to the concentration of the feed gas mixture and zero in all other void volumes unless a small bag was punctured. In that case, the small bag was assumed to contain only 0.002 m^3 of the 0.004 m^3 of the gas mixture introduced in the bag. The initial large bag VOC concentration was calculated as the number of VOC moles introduced into the large bag divided by the large bag void volume.

EXPERIMENTAL

Each lab-scale drum was a scale-down version of a U.S. Department (DOT) 17C 0.208-m^3 (55-gal) drum. The DOT 17C drum had a minimum internal diameter of 57.0 cm. A center section of the drum was removed and the two ends welded together so that the total height was 0.035 m. The drum liner has a removal lid with a metal closure ring with bolt and gasket. The dimension specifications of the liner are an outside base diameter of 0.056 m and a wall thickness of 2.3×10^{-4} m. The volume of the lab-scale drum and drum liner were measured, by filling the containers with water, to be 0.062 m^3 and 0.016 m^3, respectively. A wire support was placed inside the large bag and around the small poly bags to make it easier to prepare a large bag in each drum with a similar void volume and surface area.

The VOC concentration in a simulated waste drum was measured over a three-week period. The four small bags were initially evacuated and filled with 0.004 m^3 of a VOC-air mixture. The small bags were filled consecutively over four-minute intervals. The VOC-air mixture used in the waste drum and permeability experiments contained methylene chloride, 1,1,1-trichloroethane, and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), trichloroethylene, and carbon tetrachloride in hydrocarbon-free air. A Hewlett-Packard model

5890 Series II gas chromatograph equipped with a gas injection valve and flame ionization detector was used to determine VOC concentrations of samples collected from the simulated waste drum.

Two waste drums were placed in an environmental chamber to simulate the heating and cooling of waste drums that occur as the result of changes in environmental conditions. The daily temperature in the drum and drum liner headspace of these drums varied as a function of time. During each 24-hour period, the drums were heated for four hours during which the maximum drum temperature was approximately 45°C. Drum temperatures decreased exponentially to room temperature. In order to simplify model calculations, equations defining the measured temperature as a function of time was determined for each void volume by performing a nonlinear regression analysis of the recorded temperature data. The equations estimating actual temperatures at a given time were accurate within 0.5°C. The temperature in the drum headspace of a lab-scale waste drum maintained at ambient room temperature varied between 24.0 and 25.5°C during all trials. A constant temperature of 24.7°C was used in model calculations for the waste drums maintained at room temperature. The ambient pressure varied between 8.5×10^{-4} and 8.7×10^{-4} Pa during the experiments. A constant pressure of 8.6×10^{-4} Pa was used in all model calculations.

RESULTS

The VOC transport model was used to estimate the VOC concentration within lab-scale waste drums as a function of time. The program used IMSL subroutines to solve a series of first-order differential equations. The program was run on a CRAY X-MP 216 supercomputer. Some examples of model predictions of VOC concentrations in small bag void volumes in lab-scale waste drums maintained under different thermal environments are shown in Figs. 1 and 2. Examples of model predictions of VOC concentrations in the large bag void volumes maintained under different thermal environments are shown in Figs. 3 and 4. The accuracy of model predictions of VOC concentration in each void volume in each trial was characterized by the mean absolute relative deviation defined as

$$|\bar{d}| = \sum_{i=1}^{N} \frac{\left|\left(c_{mod} - c_{exp}\right)_i\right|}{N\, c_o} \qquad (20)$$

where

$|\bar{d}|$ = mean absolute relation deviation
c_{mod} = model prediction of VOC concentration at time t
c_{exp} = measured VOC concentration at time t
c_o = initial VOC concentration introduced into small bags
N = number of comparisons made during trial for a given void volume.

The mean absolute relative deviation for small bag, large bag, and drum headspace void volumes in each trial involving gas mixture A are summarized in Figs. 5 through 7.

In most trials, the small bag mean absolute relative deviation for each VOC was less than 2%. The large bag mean absolute relative deviation followed the same trends as observed for the small bags. The mean absolute relative deviation for the drum headspace void volume in waste drums maintained at room temperature was less than 2% for a majority of the trials. Most mean absolute relative deviations for the drum headspace void volume in waste drums maintained under a variable-temperature environment were between 2% and 4%. The increase in the deviation between the model and experimental results in the heated drums was attributed to the failure of the model to account for increased VOC solubility in the drum liner at higher temperatures.

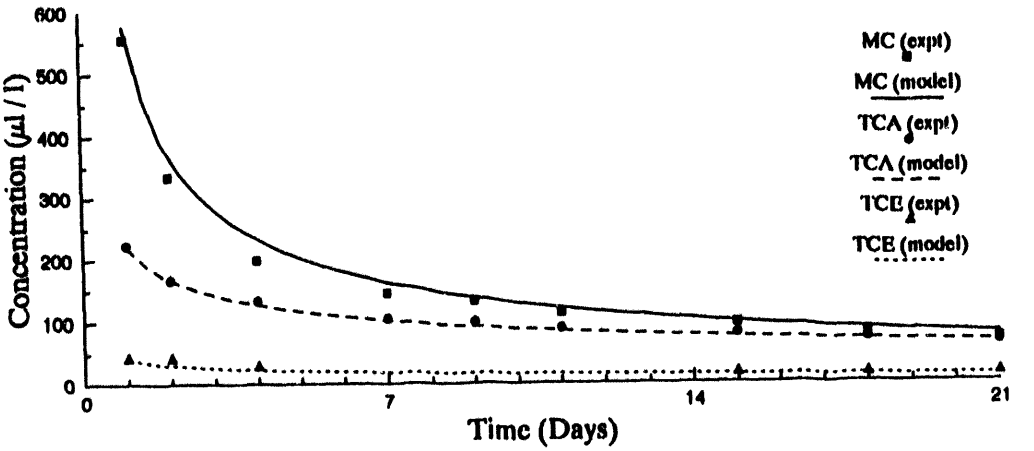

Figure 1. Model predictions and experimental data of average methylene chloride (MC), TCA, and TCE concentration in small bag void volumes of waste drum in variable-temperature environment (Trial 1.1).

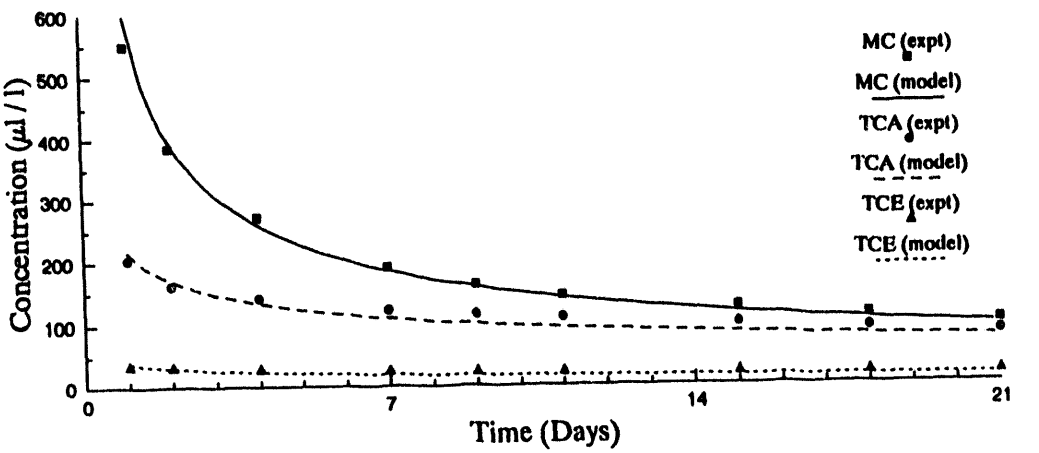

Figure 2. Model predictions and experimental data of average methylene chloride (MC), TCA, and TCE concentration in small bag void volumes of waste drum in constant-temperature environment (Trial 2.3).

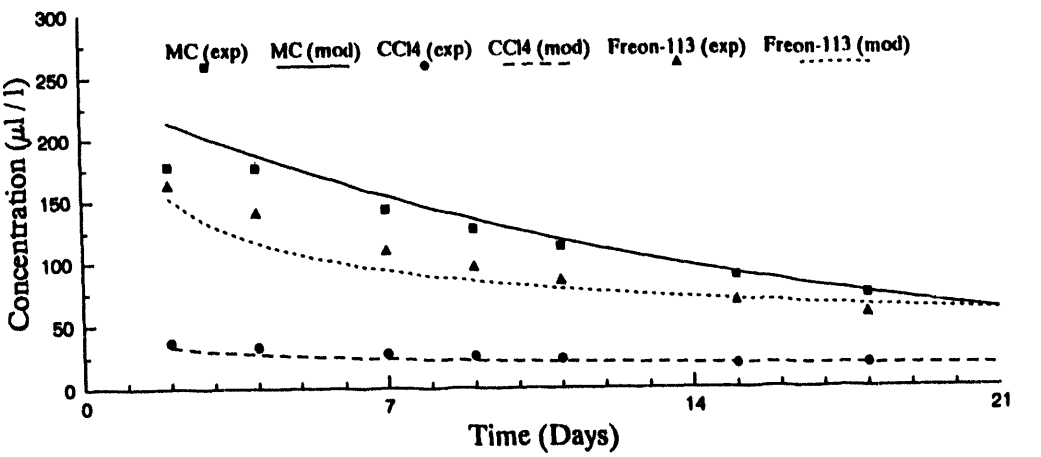

Figure 3. Model predictions and experimental data of methylene chloride (MC), carbon tetrachloride (CCl_4), and Freon-113 concentration in large bag void volume of waste drum in variable-temperature environment (Trial 2.1).

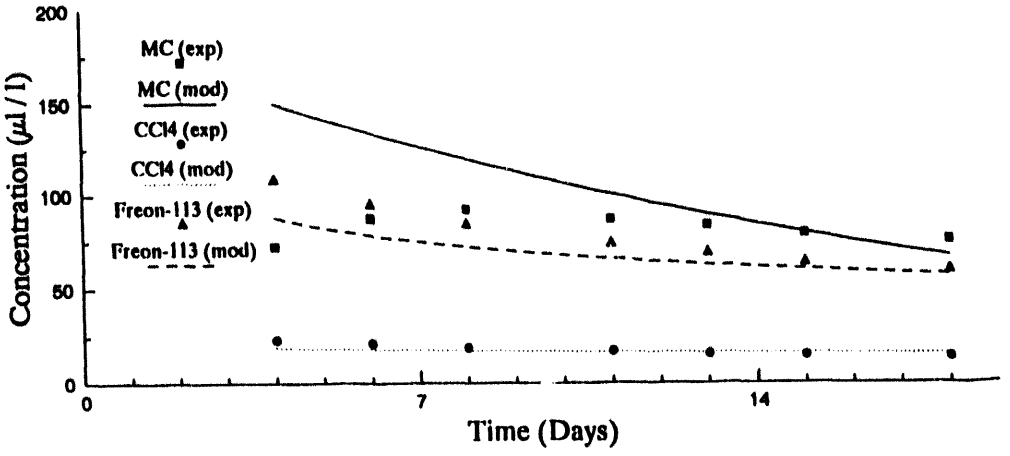

Figure 4. Model predictions and experimental data of methylene chloride (MC), carbon tetrachloride (CCl_4), and Freon-113 concentration in the large bag void volume of waste drum in constant-temperature environment (Trial 3.4).

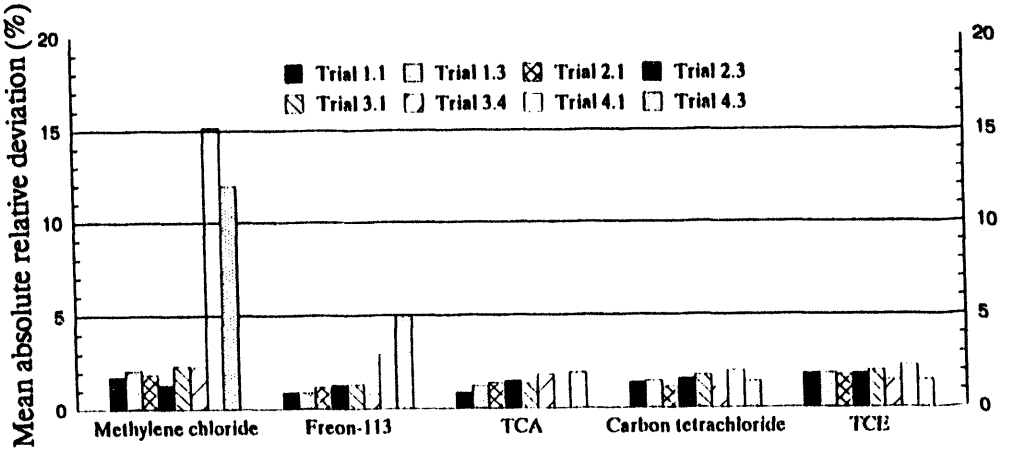

Figure 5. Mean absolute relative deviation of VOC concentration in small bags.

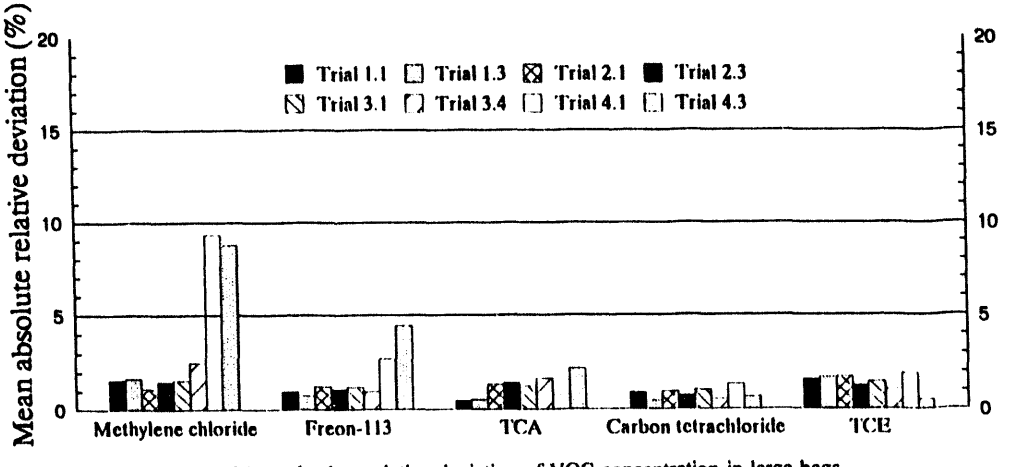

Figure 6. Mean absolute relative deviation of VOC concentration in large bags.

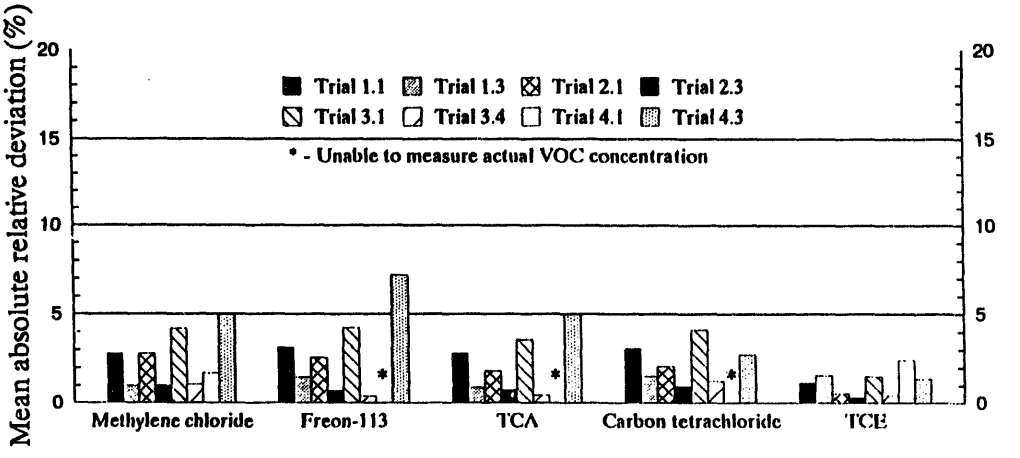

Figure 7. Mean absolute relative deviation of VOC concentration in drum headspace.

The VOC concentration in the drum headspace of waste drums maintained at room temperature was consistently greater during the course of the 3-week experiment than that in the waste drums exposed to a variable heat source. The difference was attributed to an increase of VOC solubility in the polyethylene liner at higher temperatures and an increased rate of aspiration due to fluctuating drum temperature. Although the current model does not account for the temperature dependence of VOC solubility in the polymer drum liner, the model does predict lower drum headspace VOC concentrations in a waste drum exposed to thermal cycling instead of being maintained at room temperature.

DISCUSSION

The actual bag surface area available for permeation is less than the total bag surface area. Small bags in intimate contact with each other, contact between small bags and the large bag, the large bag resting on the drum liner floor, and the overlapping and folding of the bags near the horsetail all decrease the total available surface area. The actual surface area of each bag in each drum could not be measured. For the lab-scale waste drums, the total permeable bag surface area was estimated to be 50% of the total bag surface area. The percentage of total bag surface area available to VOC permeation was estimated to the nearest 25%. Use of the total bag surface area will result in an overestimation of the rate of VOC transport from a bag.

Model assumptions of VOC solubility in the polyethylene drum liner and the empirical determination of the transfer coefficient used in equation (3) results in a model that only approximates the general effect of VOC solubility in the drum liner on VOC concentration in the drum headspace. The nature of the experiments aggravated the significance of VOC solubility in the drum liner on experimental results. The VOC capacity of a drum liner represented a significant fraction of the total VOCs introduced initially into the waste drum. Model accuracy in predicting VOC concentrations in these experiments can be improved by measuring the equilibrium VOC solubility on the polyethylene drum liner.

FUTURE WORK

A major feature of these VOC transport experiments was the transient nature of the VOC gas phase concentration as a result of having no VOC source in the waste drums. The presence of VOC-containing waste would replenish VOC molecules that had permeated and diffused out of the void volume. The presence of a VOC source in the lab-scale waste drums would more closely simulate real waste. A drum containing such waste and kept in a constant-temperature environment should reach a quasi-steady state. The effect of VOC solubility in the drum liner on the drum headspace VOC concentration should be diminished under quasi-steady state conditions. Future simulated waste drum experiments will place VOC-contaminated simulated waste in waste drums and measure VOC concentration over a relatively long period of time. The applicability of the current model to predict the VOC concentration throughout a simulated waste drum containing VOC-contaminated waste will be investigated. Finally, a model that predicts VOC concentration throughout an actual waste drum based on process knowledge and the measured VOC concentration in the drum headspace will be developed and tested.

CONCLUSIONS

A VOC transport model has been developed that accurately predicts the VOC concentration in the void volumes within a simulated waste drum. The success of the model over a variety of operating conditions indicated that the model accounted for the important transport mechanisms within the waste drum and the accuracy of model parameters. Model and experimental results have demonstrated that the primary mechanisms of VOC transport from void volumes inside a waste drum were permeation and diffusion to an adjacent void volume with lower VOC concentration and solubilization into a polymer. The model estimated the effect of temperature on VOC permeability and diffusivity but did not account for increased VOC solubility at higher temperatures. Model results demonstrated the importance of knowing the available permeable surface area. These model and experimental data will be useful in developing and testing a VOC transport model to predict VOC concentrations within actual waste drums.

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MIXED WASTE FROM A STEEL REPROCESSING SITE

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ABSTRACT. A ^{137}Cs radioactive source was inadvertently melted with scrap steel in a western U.S. steel reprocessing plant in 1990. The ^{137}Cs volatilized and was primarily collected in the particulates in the bag house. Flue dust from steel plants is a U.S. Environmental Protection Agency listed hazardous waste, KO61. About 7 BBq (200 mCi) was recovered in wastes associated with the cleanup. This paper discusses the management of this mixed waste. The repackaging, disposal, and monitoring and unrestricted release of the equipment and site are addressed.

Alternatives for disposal and processing the waste were evaluated by Rogers and Associates Engineering. The selection of alternatives focused on the possibility of Envirocare of Utah (Envirocare) obtaining a license for disposal in a mixed waste cell.

In late March of 1992 it became apparent that Envirocare would obtain licensing for disposal of mixed waste just prior to the U.S. Environmental Protection "land ban" for disposal of mixed waste, May 8, 1992. A "Movement Plan" was approved by the licensing agency and the transfer of the waste was started in early April. The material was transferred to $1 m^3$ bags using commercial truck vacuum systems. The ^{137}Cs content of each of the 700 bags of material was estimated based on measurements with radiation survey meters and an empirical algorithm.

After transport of the waste the vacuum trucks, transport trucks, and the railroad cars that had been used to store the waste were released for unrestricted release. The work area of the site was certified for unrestricted release based on residual ^{137}Cs. The basic release criterion for the site was 15 pCi/g of ^{137}Cs.

INTRODUCTION

A ^{137}Cs radioactive source was inadvertently melted with scrap steel in a western U.S. steel reprocessing plant in 1990. The source was projected to contain about 10 BBq (several hundred millicuries) and about 7 GBq (200 mCi) of the activity was recovered in wastes associated with the cleanup (1). The ^{137}Cs volatilized and was primarily collected in the particulates in the bag house. Flue dust from steel plants, termed "emission control dust," is a U.S. Environmental Protection Agency (EPA) listed hazardous waste, KO61 (2). The plant was shut down when the contamination was detected and the contamination was cleaned up immediately to allow the site to return to operation. However, since the material was "mixed waste," there was no viable disposal option and the 610 metric tons of waste was temporarily stored on site, under an amended radioactive materials license. Alternatives for disposal and processing the waste were evaluated by Rogers and Associates Engineering (RAE) (3). The selection of alternatives focused on the possibility of Envirocare of Utah (Envirocare) obtaining a license for disposal in a mixed waste cell.

This paper discusses the management of this mixed waste. The repackaging, disposal, and monitoring and unrestricted release of the equipment and site are addressed. The criteria for unrestricted release of the site are presented.

Background

The wastes from the cleanup of the site included flue dust from the filters for the furnaces, the fabric filters from the furnace bag house filters, soil and asphalt, and vacuum hoses and other materials used during the cleanup activities. These materials contained ^{137}Cs from the melted source and residual flue dust. The flue dust, a listed hazardous waste KO61, contained metals from the foundry and furnace operations. The primary toxic constituent in the flue dust was lead (about 2%), however other metals were also present. Tests by the owner had indicated that it was extremely hard to treat the flue dust so that it would pass the EPA leachability tests for toxicity.

The flue dust is normally used as the base for fertilizer pellets, and does not have to be disposed of as a waste. Because of the contamination with ^{137}Cs, it could not be used and became a mixed waste. There are no specific regulations for acceptable, or below regulatory concern, concentrations of ^{137}Cs in materials such as fertilizer. Because of the uncertainties of processing the material and the lack of regulatory guidancer, the owner decided not to try to sell or give the material to other sources, or to try to process the material to reduce the concentration and then identify other use or disposal alternatives.

CHARACTERIZATION

The waste from the cleanup operations was stored in eight condemned railroad cars (i.e., cars no longer acceptable for use on railroads) at the steel plant site. Loose materials, including flue dust and debris from the cleanup were placed in seven railroad hopper cars, which each had three hoppers. The hoppers, about 2.4 m by 4.3 m and 3 m deep had a nominal volume of about 3 m^3. The volume and weight of material varied, but averaged about 100 metric tons per car. Cleanup debris, fabric filters, and drums of material were stored in a box car. The discharge chutes of the hopper cars and the doors of the box car were welded shut to isolate the material during the storage period.

RAE sampled the waste in the hopper cars to characterize the radiological composition. It was anticipated that the waste could be disposed of in the proposed Envirocare mixed waste facility, when the facility obtained its mixed waste license. The mixed waste license, which was anticipated for approval in about August 1991, was to be granted by the State of Utah under agreement state authority. The mixed waste license required Utah granting licenses/permits under authority related to both 10 CFR 61 for radioactive low-level waste (LLW) and 40 CFR 260 for hazardous waste. The proposed Utah license for LLW had a concentration limit of 21 Bq/g (560 pCi/g) for ^{137}Cs (4). Most of the waste was flue dust or frit (processed flue dust). The flue dust is a very fine grained easily dispersed material (micrometer size). Frit, an intermediate process in producing fertilizer, is pellets formed by adding oil mist and compressing the flue dust. The pellets have a nominal diameter of 1 to 2 mm.

Three samples were obtained from most of the hoppers, or 21 samples per car, as specified by the sampling plan. A total of 57 samples were obtained, since several hoppers were empty or almost empty. The samples were collected using a 1 m tube sampler, when the sample could be retained. Each sample represented about 3 aliquots of the vertical extent of the waste. The samples were analyzed by gamma spectroscopy to determine the variation of the concentration in a hopper and the average concentration.

Table 1 provides a summary of the data on radioactivity and the weight of material in the individual hoppers. The estimated weight of material in each hopper was based on the dimensions of the hopper, the degree to which a hopper was filled, and estimated densities of the material. The density of the materials was estimated from the net weight of material in the car and the related volume of material.

Table 1. Mixed waste.

Rail Car	Hopper	Waste (Mt)	^{137}Cs Activity in Waste (Bq/g)	(GBq)
1	A	45	1.6	0.07
	B	39	48.1	1.89
	C	42	42.5	1.78
2	A	29	0.1	0.04
	B	16	1.3	0.04
	C	36	1.4	0.04
3	A	29	5.2	0.15
	B	33	14.1	0.48
	C	36	20.7	0.74
4	A	51	2.0	0.11
	B	8	1.8	0.04
	C	53	2.2	0.11
5	A	12	0.3	0.04
	B	42	3.1	0.11
	C	42	35.1	1.48
6	A	15	0.7	0.04
	B	24	1.3	0.04
	C	22	1.0	0.04
7	A	18	1.8	0.04
	B	0		0.00
	C	21	0.9	0.04
Ave./Total All Cars		614	11.5	7.10

The weighted average concentration of the material (i.e., summation of weights times concentrations, divided by total weight) was 11 Bq/g. The average was about 55% of the proposed license limit for Envirocare (1). However, the concentration in some hoppers ranged up to 50 Bq/g, more than twice the Envirocare anticipated license limit of 21 Bq/g. Therefore, since each load of material arriving at Envirocare has to be within the license limit, it was evident that detailed loading plans would be necessary and there would have to be detailed radiation monitoring of the waste in order to properly load vehicles.

MOVEMENT PLAN

In late March of 1992 it became apparent that Envirocare would obtain licensing for disposal of mixed waste just prior to the U.S. Environmental Protection "land ban" for disposal of mixed waste. A "Movement Plan" was submitted to the regulatory agency on March 16, 1992, for repackaging the waste and disposal at the Envirocare mixed waste cell (5). The plan provided for removal of the material from the hoppers of the railroad cars using commercial truck-mounted vacuums, packaging it in 1 m^3 polypropylene bags with polyethylene liners, and planning the loading of transport vehicles to ensure shipments would meet the Envirocare license requirements. The State of Utah, the licensing agency for

Envirocare, required that the plan include special consideration for the potential dispersion of the flue dust. Envirocare specified that the material delivered to the site be within 5% of the moisture required for optimum compaction.

The Movement Plan and activities for implementing the plan included preparing a Health and Safety Plan, removal of the mixed waste from the railroad cars using truck-mounted vacuums, direct placement of the waste in 1 m^3 polyethylene bags, sometimes known as sling bins, radiation monitoring and sampling of the bags to determine the concentration of ^{137}Cs in each bag, and developing loading plans for the transport of the material to Envirocare. To meet the moisture requirements, samples were taken to check the range of moisture in the stored waste and a system was designed for injecting water into the sling bins while the waste was being discharged to them. The moisture content of the stored waste ranged from less than 1% to about 23%, for one bin where precipitation had leaked in. The Health and Safety Plan included specifications of radiation monitoring during the removal and repackaging, personnel protection equipment and procedures, and providing health and safety training for personnel. All personnel were required to wear thermoluminescent dosimeters (TLD) to monitor radiation exposures.

The prior waste characterization indicated that the concentrations of ^{137}Cs in the hoppers were not uniform. Therefore, in order to allow loading the waste for shipments to Envirocare it was necessary to have reasonable estimates of the average content of ^{137}Cs in each package of waste. Based on the ^{137}Cs concentration and weight of each package, it would then be possible to develop loads that would meet the Envirocare license concentration limits.

The concentration of ^{137}Cs was based on measurements with 1-inch NaI detectors and radiation instruments with scalers (e.g., Ludlum Model No. 2220). The algorithm for relating radiation measurements to the ^{137}Cs concentration was initially based on results from the shielding code Microshield (6). The Microshield code was used to estimate the radiation exposure rate at 2 cm from the surface of a 1 m^3 source. The calculated exposure rate and calibration detector response factors were used to determine the detector response per unit of ^{137}Cs concentration. The calibration factor was 2,700 counts per minute (cpm) per Bq/g (100 cpm per pCi/g).

REMOVAL OF WASTE AND RELEASE OF SITE

The waste was removed from the hoppers of the railroad cars using commercial truck-mounted vacuums. One to two personnel entered the hopper for the removal operations. All personnel working directly with the waste had Occupational Safety and Health Administration related 40-hour safety training (7) and received on-site radiation safety training.

The waste was directly discharged from the vacuums into the sling bins. After the sling bins were closed they were monitored using a NaI radiation detector. Measurements were taken against the bags on all four sides and on the top. Generally the average of the five readings (net above background) was used to determine the ^{137}Cs concentration based on the calibration factor. The background readings were based on the background in the area, which was generally about three times the normal background for the NaI detector, due to the presence of the waste. For partially fully sling bins the reading from the top of the bag was generally used to provide a conservative estimate. If the bag was not full the geometry of the waste from the top was generally a 1 m^2 source, whereas the sides represented a source of a fraction of a square meter. Since the calibration factor was based on a 1 m^2 source, the reading at the top was the most applicable measurement.

Samples of the waste were taken from fifty bags and analyzed for ^{137}Cs. The results of these measurements were used to confirm the calibration factor determined from the Microshield code calculations. The calibration factor was only adjusted by 2% based on the empirical sample results, verifying the validity of

the factor derived from the Microshield code.

The removal of waste from the railroad cars was started on April 6, 1992. Envirocare had not received final approval of mixed waste license yet and the repackaged waste had to be stored at the steel facility site. Interim approval was received on April 14, 1992, to ship the waste to the Envirocare site. The waste was shipped in end-dump trucks, with the load covered with tarps, with net payloads of about 20,000 kg (44,000 lb). The shipments were manifested for hazardous waste, and the trucks were placarded (U.S. Department of Transportation or DOT 9189) to denote the KO61 waste. The shipments were below the DOT criterion for radioactivity (i.e., 2 nCi/g or 74 Bq/g) (8) and were not radioactive waste shipments.

Radiation monitoring of airborne emissions and personnel monitoring indicated there was minimal radiation exposure to the personnel performing the work for the project. All TLD results were below 0.01 mSv (10 mrem), the reporting limit for the TLD service.

Thirty-eight truck shipments of waste were delivered to Envirocare. About 720 metric tons of waste, with an average concentration of 10 Bq/g were delivered. The final estimates included several tons of material from final cleanup of the site and the values are well within the uncertainties of the estimates from initial characterization of the waste. The cost of this phase of the project, including disposal of the waste was about $1.5 million.

UNRESTRICTED RELEASE OF EQUIPMENT AND THE SITE

Residual waste was removed from the railroad cars used to store the waste, the vacuum trucks, and the areas of the site used for the waste removal. After removal of residual contamination the areas were monitored for residual contamination and sampled to verify cleanup to criteria for unrestricted release.

Criteria for Unrestricted Release

The release criteria for equipment (specified by licensing agency) was based on U.S. Nuclear Regulatory Commission (NRC) Regulatory Guide 1.86 (9). The basic criteria for ^{137}Cs, a beta emitter, is 5,000 disintegrations per minute (dpm) per 100 cm^2 area, based on averaging over an area of 1 m^2. The maximum contamination in small areas of 100 cm^2 or less must be less than three times the criterion for the average. The criterion for removable surface contamination was 1000 dpm per 100^2.

There are no regulations or statutory guidance for the concentration of ^{137}Cs for unrestricted release of soil. Radiological assessments of ^{137}Cs contamination indicate that the primary risk from exposure of radiation in the environment, at an industrial site, is exposure to external gamma radiation (10,11,4). Based on assessments using the Microshield computer code (6), a concentration of 0.55 Bq/g (15 pCi/g) in the surface 15 cm of soil results in a dose rate of about 0.05 μSv (5 μR/hr) per hour, or 0.1 mSv per year based on a 2000 hour occupational year of exposure. For conservatism, the above calculation does not include adjustments for the difference between exposure rates in roentgen and doses or the effective whole body dose (EDE) versus air dose. Based on an exposure for 30 years and a radiation risk factor of 4×10^{-5} fatal cancer risk per mSv (12); the dose of 0.1 mSv per year relates to a risk of one per 10,000. The risk factor of 4×10^{5} per mSv (400×10^{-6} per rem) is based on the concept of no threshold for radiation effects, linear extrapolation of risks from high doses, and a reduction factor of two for reduced effects at low dose rates (12). The lifetime risk of one per 10,000 is taken as one of the criterion from the National Contingency Plan for cleanup of Superfund sites (13). The derived criterion of 0.55 Bq/g (15 pCi/g) is also the criterion specified for the cleanup of the Safety Light site in Bloomsburg, Pennsylvania (14). The release criteria are summarized in Table 2.

Table 2. Cleanup criteria.

Application	Criterion	Comment
Surface Contamination on Equipment		
-Total, ave.	5,000 dpm/100^2	NRC Reg. 1.86 (9)
-Maximum	15,000	
-Removable	1,000	
Residual ^{137}Cs in soil	0.55 Bq/g (15 pCi/g)	NRC guidance (14)
	0.1 mSv/yr (10 mrem/yr)	Relates to 0.55 Bq/g
	10^{-4} lifetime risk	Relates to EPA NCP Superfund guidance and 0.55 Bq/g.

Unrestricted Release of the Railroad Cars and Vacuum Trucks

The railroad cars and vacuum trucks were cleaned using clean sand after completion of the waste removal. A low pressure sprayer was used to spray the interior surfaces of the cars with a sand/water jet. The material was then removed by the vacuum trucks, and the sand/water mixture also cleaned the vacuums on the trucks as it passed through the vacuums. The fabric filters and vacuum hoses for the vacuum trucks were disposed of as radioactive waste.

The railroad cars and vacuum trucks were monitored with G.M. pancake probes for surface contamination and smears were taken to measure for removable contamination. The vacuum trucks and railroad cars were released, after it was verified that they met the stated criteria for unrestricted release. The railroad cars were then melted as scrap steel in the mill.

Unrestricted Release of Site

After the waste had been removed from the site, the work areas were surveyed with NaI scintillation detectors to identify areas of residual ^{137}Cs contamination from the waste transfer operation. About 3 yd^3 of soil were excavated to remove surface contamination.

Soil samples were collected from the work areas to validate the final cleanup of the work areas. A sample, composed of 5 aliquots (located like the spots on a die) was taken from each 100 m^2 area. The samples were taken to a depth of 15 cm, except in areas where rocks interfered with sampling. The radiation surveys and the analytical results from the sampling indicated that areas were generally cleaned up to less than 0.2 Bq/g, with maximum residual ^{137}Cs of 0.55 Bq/g, and gamma dose rate less than 0.1 μGy per hour due to residual ^{137}Cs. It was recommended the site be released for unrestricted use, based on the residual ^{137}Cs activity.

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CHAPTER 6

Regulatory Issues: Site Specific Topics

CONCRETE AS SECONDARY CONTAINMENT FOR INTERIOR WALL EMBEDDED WASTE LINES

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ABSTRACT. Throughout the Department of Energy complex there are numerous facilities that handle hazardous and radioactive waste solutions. Due to the hazardous constituents of the mixed waste, secondary containment of tank systems and their ancillary piping, in accordance with Resource Conservation and Recovery Act, is a concern for such existing facilities. The Idaho Division of Environmental Quality was petitioned in 1990 for an Equivalent Device determination regarding secondary containment of waste lines embedded in interior concrete walls. The petition was granted; however, it expires in 1996. To address the secondary containment issue, additional studies were undertaken. One study verified the hypothesis that an interior wall pipe leak would follow the path of least resistance through the naturally occurring void found below a rigidly supported pipe and pass into an adjacent room where detection could occur, before any significant deterioration of the concrete takes place. Other tests using acidic waste solutions demonstrated that rebar and construction joints are not an accelerated path to the environment. The results of these latest studies confirm that the subject configuration meets all requirements of secondary containment.

INTRODUCTION

The use of concrete as a material of construction for primary or secondary containment has wide application. Various guidance documents for hazardous waste tank systems include concrete as a compatible material for certain waste types. The U.S. Environmental Protection Agency's (EPA) technical resource document for hazardous waste tank systems(1) indicates that generally two types of concrete can be used for liners: traditional mass-poured concrete, if sufficient reinforcing steel is used to control cracking and, concrete that is prestressed or post-tensioned. It further notes that a secondary containment liner or material of construction must be compatible with its contained waste(s) to ensure the containment's integrity, thus preventing releases to the surrounding environment. Numerous types of aggregates, additives, and other parameters affect concrete's resistance to chemical attack. Consequently the owner or operator must use detailed chemical and physical analysis of contained waste(s) along with information and/or test results to ensure compatibility of a stored waste with its secondary containment.

When hazardous waste lines pass through an interior concrete wall, the wall, in addition to the building, is typically considered to provide secondary containment. However, very little technical literature addresses the compliance aspects of this practice. The purpose of this paper is to address the secondary containment aspects of acidic waste lines embedded in interior concrete walls with regard to EPA and other compliance standards. The data are from a variety of sources, ranging from technical publications of the American Concrete Institute to results from a series of tests and experiments of a specific configuration.

CONFIGURATION

Figure 1 illustrates the basic configuration that was the subject of a series of studies. This configuration is typical of numerous nuclear facilities built in the 1950's by the Atomic Energy Commission, now known as the Department of Energy (DOE). Either side of the thick shielding wall is a room or cell lined with a waste- compatible material, such as stainless steel, with leak detection and accumulated liquid removal capabilities. The basic concrete studied was the mass-poured, Class C, reinforced concrete specified in 1951 vintage specifications(2). The major characteristics of the concrete are summarized in Table 1. The waste solution for which compatibility of the concrete was tested was acidic in nature, ranging from .1N HNO_3 to 10N HNO_3, including mixtures of HNO_3/HF.

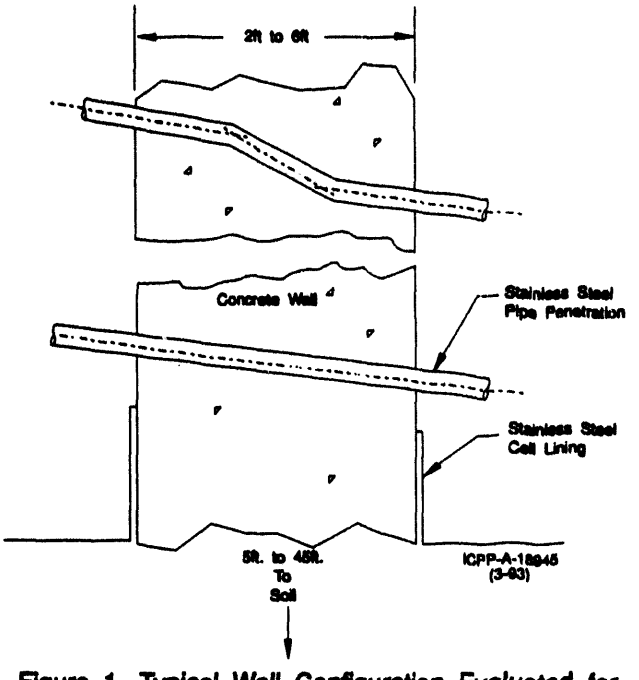


Figure 1. Typical Wall Configuration Evaluated for Secondary Containment.

REGULATORY REQUIREMENTS

In order to assess the adequacy of a secondary containment configuration, it is necessary to have an understanding of the purpose of the secondary containment, and the function which the containment needs to perform.

The Resource Conservation and Recovery Act (RCRA) was enacted to ultimately protect the environment. Specifically dealing with hazardous waste tank systems (including ancillary piping), 40 CFR 265.193 (3) states: "In order to prevent the release of hazardous waste, or hazardous constituents to the environment, secondary containment that meets the requirements of this section must be provided..."

Table 1. Major characteristics of the concrete of figure 1

Type I cement

Minimum 28-day compressive strength of the concrete: 3750 psi
Maximum water content: 5-1/4 gallons per sack of cement
Course aggregate: 3/4 inch maximum size, well graded gravel, mostly basalts and thermally metamorphosed sedimentary rock
Maximum compacted volume of aggregate per volume of cement: 3-1/2
Slump range: 1-3 inches
Ratio of fine to total aggregate based on dry compacted volume: 35-50%
Concrete placement: Two foot thick lifts
High frequency internal vibration used
Reinforcing: #6 reinforcing steel bars spaced at 15 inch on centers both horizontally and vertically

Two general requirements are outlined in paragraph(b) of 40 CFR 265.193. Secondary containment systems must be:

(1) Designed, installed, and operated to prevent any migration of wastes or accumulated liquid out of the system to the soil, groundwater, or surface water at any time during the use of the tank system; and
(2) Capable of detecting and collecting releases and accumulated liquids until the collected material is removed.

To meet the requirements of paragraph (b), specific minimum criteria for secondary containment systems are given in paragraph (c) of 40 CFR 265.193. These can be summarized as follows:

(1) Constructed of or lined with materials that are compatible with the wastes.
(2) Placed on a foundation or base capable of providing support to the secondary containment system.
(3) Provided with a leak detection system that is designed and operated to detect the failure of the primary or secondary containment.
(4) Sloped or otherwise designed or operated to drain and remove liquids resulting from leaks, spills, or precipitation.

Each of these specific design criteria will be addressed relative to the configuration that was studied.

CRITERIA 1 AND 2 - MATERIAL COMPATIBILITY AND STRUCTURAL INTEGRITY

This section will discuss the capability of the concrete around the stainless steel interior wall penetration to provide adequate containment to protect the environment and to direct the leak into the lined cells for detection and removal.

To provide a framework for this discussion, it is necessary to define the meaning of "compatible." Because an explicit definition is not included in the regulations, the following definition is implied and used as the basis for this work: "Materials which are compatible with the wastes" means a material whose function will not be degraded or compromised by contact with the waste.

This definition is the only practical interpretation of the explicit regulatory definition of "incompatible waste" found in 40 CFR 260.10 (4), which states that an "incompatible waste means a hazardous waste

which is unsuitable for placement in a particular device or facility because it may cause corrosion or decay of containment materials."

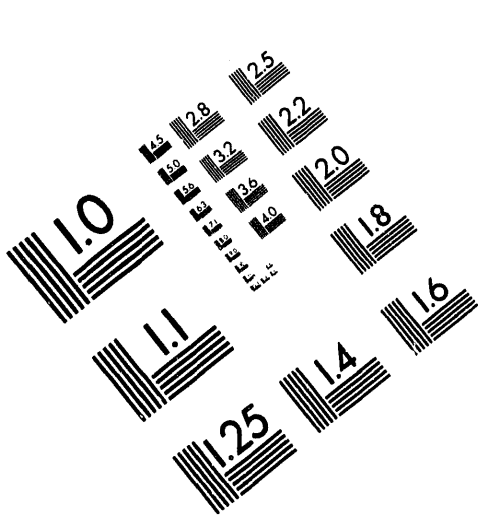
From a practical standpoint, all construction materials corrode and decay over time as a result of contact with process or waste solutions and environmental conditions. Selecting the proper construction materials for a specific application requires materials with acceptably low rates of corrosion. It will be shown that the corrosion rate of concrete by acidic waste around the interior wall penetrations is so low that it can be considered "compatible."

A number of tests have been performed by the Portland Cement Association (PCA), Phillips 66, and the Westinghouse Idaho Nuclear Company, Inc. (WINCO) to establish the rate of penetration or disintegration of concrete or mortar materials made with portland cement when exposed to acidic solutions. Table 2 summarizes the results of the various tests, which range from mortar coupons immersed in solutions to concrete blocks exposed to static soaking tests as well as dynamic movement of solutions across the concrete.

Table 2. Summary of compatibility tests.

Year	Test Agency	Acid Concentration	Average rate of surface loss (in./hr)	Type of test
1962	Phillips 66(5)	0.7 N HNO_3	0.0027 to 0.003	concrete coupon immersion
1966	PCA(6)	0.1 N HNO_3	0.00004	mortar coupon immersion
1966	PCA(6)	10 N HNO_3	0.0025	mortar coupon immersion
1989	WINCO(7)	3.1 N HNO_3/HF	0.0034	mortar coupon immersion
1990	WINCO(8)	3.1 N HNO_3/HF	0.00014	pipe embedded in concrete cylinder
1990	WINCO(9)	3.1 N HNO_3/HF	0.0002	pipe pressfit in concrete cylinder
1992	WINCO(10)	4 M HNO_3	0.0002 to 0.0015	static and dynamic tests on concrete cylinders

Reviewing the pre-1992 data, Wiss, Janney, Elstner Associates, Inc. (WJE) concluded that the resultant concrete loss from a leaking pipe embedded in an interior wall would not create any significant concern, relative to the function of the concrete (11). This conclusion was reinforced by a study performed by North Carolina State University (NCSU) (12). The NCSU study included leakage tests on laboratory-produced wall assemblies patterned after Fig. 1. An embedded pipe, with pre-drilled holes (1/4 inch diameter), was allowed to leak 4 M nitric acid over an extended period of time (34 days). As with other tests, the rate of attack decreased over time. The wall assembly was sectioned and examined. The area affected by the leak was limited to a depth of 0.5 inch, with a radial spread about the hole in the pipe/concrete interface of less than 2.5 inches (Fig. 2). The 34 day exposure time was well beyond the time period during which a leak



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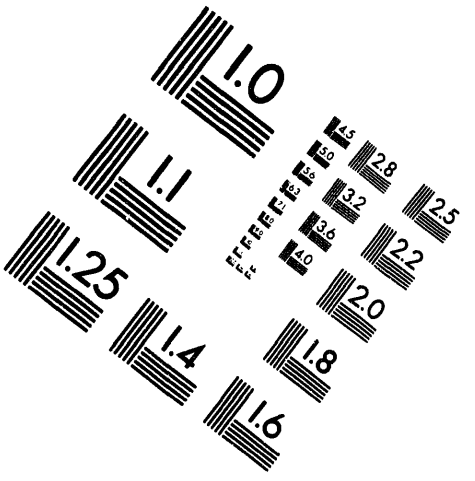

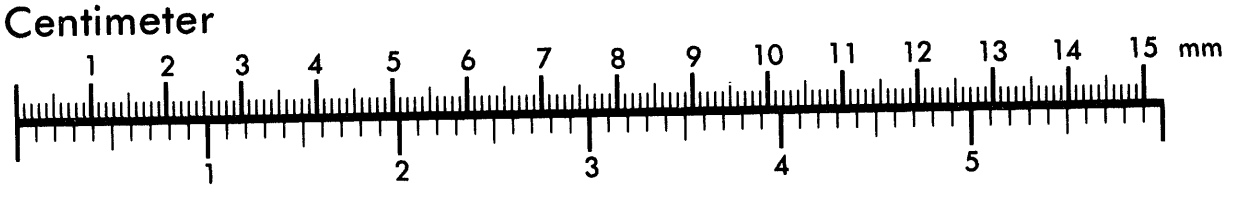

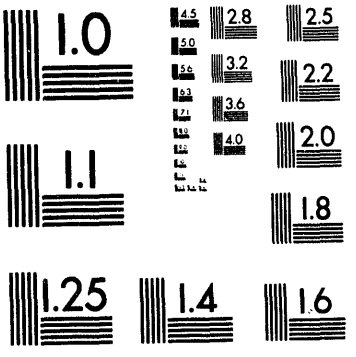

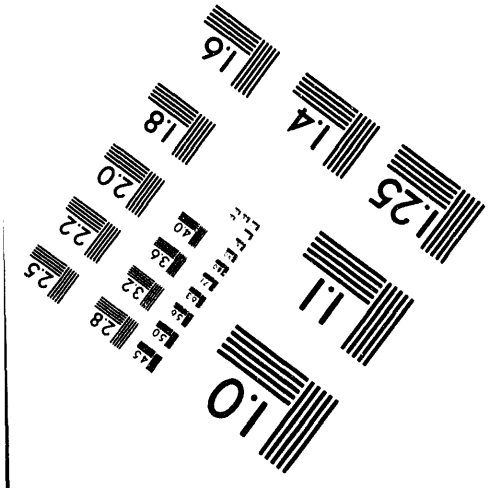

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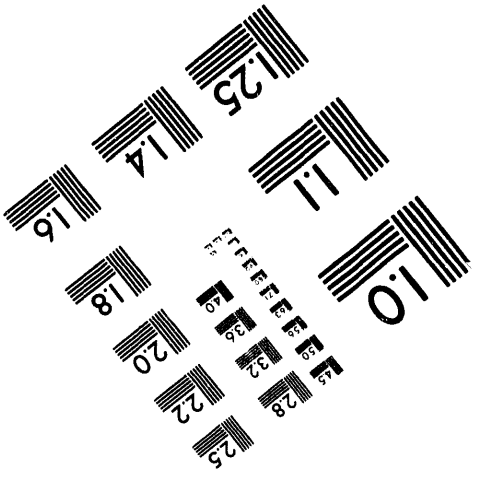

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would be detected and secured (generally within 24 hours). The NCSU study showed that for the conditions studied, the acidic leak would not significantly affect the concrete before a leak could be detected.

The 1992 study performed by WINCO was designed to address whether an acidic leak in the vicinity of carbon steel rebar or a construction joint would have an accelerated path to the environment or have an effect of structural concern. The test configuration shown in Fig. 3 was used in both a static mode and with the acid supply continually stirred and replenished. For the static situation, it was found that once the initial acid charge was consumed, the attack on the rebar essentially stopped. It was shown that in the dynamic situation, once the rebar is consumed to a depth of about 2 inches, the "dead leg" becomes equivalent to the static scenario. Acid penetration into the construction joint proceeded 0.25 inches and then stopped. In both situations, the reaction products first hindered and then essentially stopped the progressive attack of the rebar and the concrete. This study clearly demonstrates that construction joints and rebar do not provide an accelerated path to the environment.

From a secondary containment standpoint the function of the concrete in the Figure 1 configuration is to prevent the migration of any wastes or accumulated liquid out of the system to the soil, groundwater, or surface water. The above studies provide empirical evidence that the concrete's ability to perform its secondary containment function is not degraded by exposure to an acidic leak. Hence the first specific criteria, compatibility of the secondary containment with the waste, is satisfied by the subject configuration. Regarding the second specific criteria for secondary containment, the foundation or support for the secondary containment, it is obvious that the concrete structure itself provides the support for the secondary containment. The results from previous tests and more recent studies support the conclusion that the structural integrity of the concrete wall is not significantly affected by a leak from an embedded waste line.

CRITERIA 3 AND 4 - LEAK DETECTION AND REMOVAL OF ACCUMULATED LIQUIDS

This section will demonstrate that the subject configuration of waste lines embedded in interior concrete walls meets the requirements for ensuring leak detection and liquid removal. A leak that originates in the embedded penetrations will be channeled to the cell wall surface, down into the lined cell, and into a sump where it will be detected. The focus of this paper is on the path from the interior wall leak to the wall surface.

When concrete sets around a rigidly supported member, such as a pipe penetration, a void commonly occurs between the concrete and horizontal sections of the pipe and/or reinforcing bar. This void or separation between the pipe and the concrete will provide a conduit for liquids wastes, should the waste line develop a leak within the concrete wall.

This void resulting from concrete subsidence is commonly recognized by the concrete industry and has led to special design considerations for selected applications. A 1989 American Concrete Institute (ACI) report(11) discusses this type of void:

> After initial placement, vibration, and finishing, concrete has a tendency to continue to consolidate. During this period, the plastic concrete may be locally restrained by reinforcing steel, a prior concrete placement, or formwork. This local restraint may result in voids and/or cracks adjacent to the restraining element (Fig. 1,2,4).

A 1987 ACI report (12) states that it is "nearly impossible to eliminate air voids from inwardly sloping formed surfaces" and that subsidence of the concrete occurs when the "concrete mechanically settles at or near initial set." These two phenomena occur under piping that is rigidly supported during the casting operation, which is the case with the subject configuration illustrated in Fig. 1.

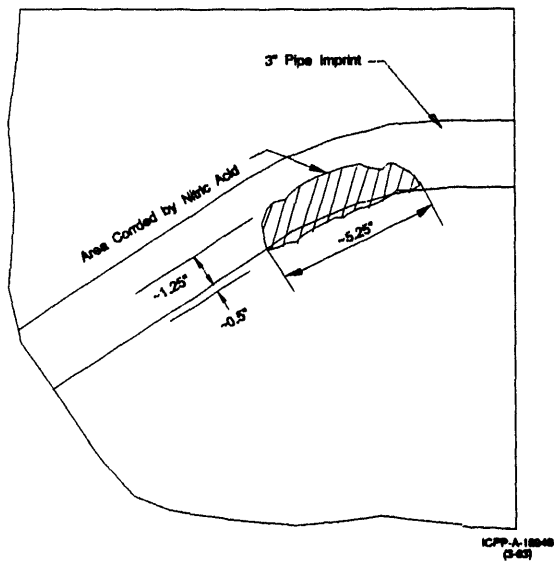

Figure 2. Approximate Size of Corrded Area of Concrete Exposed to a Continual Interior Wall Leak for 34 Days

Numerous design and construction practices have been tailored to address this phenomenon. Proper form design (ACI 347) and adequate vibration, provision of a sufficient time interval between the placement of concrete in columns and the placement of concrete in slabs and beams (ACI 309.2R), the use of the lowest possible slump, and an increase in concrete cover will reduce settlement cracking. Tightly fitted washers at the midpoint of tie rods are included in the design of liquid retaining structures, such as tanks (ACI 350). Concrete tanks without the washers on tie rods commonly leak along the rods due to the natural subsidence of concrete under the tie bar. Various concrete codes (ACI 349, ACI 318, ACI 343) require that "top" reinforcing bars, which have 12 or more inches of concrete below the bar during placement of the fresh concrete, require a development length 40% greater than basic development length for bars with less than 12 inches of concrete below the bar. This requirement is based on numerous laboratory tests that show that the subsidence of concrete below such bars produces a void under the bar that reduces the bond strength between the steel and concrete (11).

The above examples from the technical literature establish that the void under a rigid member is a recognized phenomonen. Leak detection via the subsidence under rigid piping has occurred at a facility with a configuration typified by Fig. 1. The main nuclear fuels reprocessing facility (CPP-601) at the Idaho

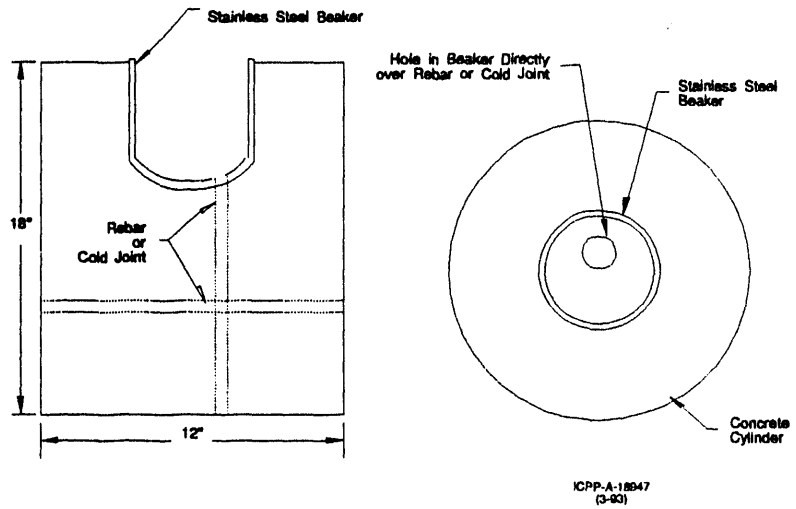

Figure 3 Test Configuration for Rebar/Cold Joint Testing

Chemical Processing Plant (ICPP) was built in the early 1950's under the auspices of the Atomic Energy Commission. In 1984, a 3/4 inch process line for an evaporator developed a leak inside a 3 foot thick wall. The leak was discovered via a sump level alarm in the adjacent cell. The source of the leak was determined by noting that the sump level increases occurred immediately after start-up of the evaporator initiated steam condensate flow through the embedded line. A similar situation occurred and was detected (1984) in a 1/2 inch process sample line passing through a 5 foot thick concrete shielding wall.

The foregoing information demonstrates that the subject configuration meets the specific RCRA secondary requirement for leak detection. Because of the naturally occurring void that forms in concrete below a rigid member, a flow path to the wall surface exists for an interior wall pipe leak. Once leakage reaches the wall surface, it can be detected either by visual means or by collection in a sump. The specific criteria for removal of accumulated liquids can be met in many different ways once a leak reaches the wall surface.

REGULATORY CONCLUSIONS

As demonstrated, it is clear that the examined configuration meets all of the specific design criteria delineated by RCRA for secondary containment. The concrete was demonstrated to be compatible with the acidic waste in that the waste does not affect the containment's integrity, thus preventing releases to the surrounding environment. As indicated in Ref. 1 relative to hazardous waste tank liners, the advantages of using concrete for secondary containment include its durability, structural integrity, layout flexibility, and the ease of integrating structural support. The concrete wall, along with its reinforcing, provides a foundation or base capable of providing support to the secondary containment system.

The naturally occurring void that forms under a rigid member as the concrete consolidates provides a direct

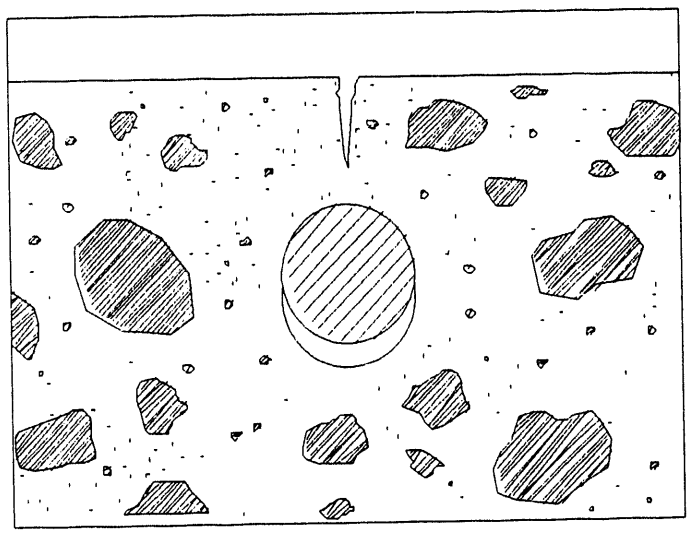

Figure 1.2 Crack Formed Due to Obstructed Settlement

Figure 4. - Figure 1.2 From 1989 ACI Committe 224 Report Illustrating Natural Subsidence of Concrete Below a Rigid Member

path from an interior leak to the wall surface. This aspect of the configuration, combined with a leak detection system in the adjacent cell or room, provides the ability to detect a failure of the primary containment. This naturally occurring void also accommodates the criteria to drain and remove liquids resulting from leaks.

By meeting the specific criteria, the general requirements of secondary containment are also met. The test results show that rebar and construction joints are not accelerated paths to the environment, that in this application, the concrete is compatible with the acidic wastes and that a path to the wall surface for leak detection exists. Therefore, any migration of wastes or accumulated liquid out of the system to the soil, groundwater, or surface water will be prevented. The natural conduit under each pipe ensures that the system is capable of detecting and collecting releases and accumulated liquids until the collected material is removed.

APPLICABILITY

Although the studies reported in this paper focus on one configuration and one waste stream, the results can be easily applied to other configurations and waste streams. The studies identify key parameters that must be considered when evaluating the secondary containment status of concrete.

In general, the vulnerability of concrete to chemical attack results from three of its characteristics: permeability, alkalinity, and reactivity. To evaluate the applicability of the results reported in this paper to other configurations these three characteristics and factors affecting them should be considered. For example, the concrete studied was based on a 1950's vintage specification. Advances in concrete design and production, chemical additives, and admixtures improve the workability and placement, enhance durability, and reduce permeability. Consequently, the test results could conservatively be extended to modern concrete structures. Other vintage structures would need to be evaluated for parameters that would affect characteristics such as crack control, resistance to chemical attack (nature of the aggregate), slump, size of penetrations, as well as the lack of major structural cracks. It should be noted that the laboratory conditions associated with wall assembly tests represent the optimum situation for minimizing the magnitude of the pathway for a given size of pipe. Actual conditions, reasonably expected in the field, would result in a greater amount of subsidence than that experienced in the laboratory study. The laboratory study confirmed that a leak path for leak detection exists, even with less subsidence then would be expected in the field.

In most cases, extending the results of this paper to other waste streams is a simple matter of consulting any number of publications on the resistance of concrete to chemical attack (15,16). In Reference 14, nitric acid is indicated to disintegrate concrete rapidly. Obviously concrete would not be selected as a primary containment where an unlimited supply of fresh acid would disintegrate the concrete rapidly. However, the studies summarized in this paper demonstrate that concrete is an acceptable secondary containment material even for nitric acid. This is due to the fact that in the secondary containment situation studied, the acid (from a pipe leak) in contact with the concrete is not totally replenished and consequently the concrete does not disintegrate rapidly. Therefore Reference 15 or 16 would provide a relative measure for compatibility and would be a simple indication of the applicability of the results of this paper. A designator less severe than "disintegrates rapidly" for a solution would indicate applicability.

In summary, the technical justifications for concrete as secondary containment for embedded acidic waste lines can readily be applied to hazardous and mixed waste lines at commercial, DOE, and other federal facilities. The potential application can be easily assessed for both existing facilities, new facilities, and non-acidic waste streams.

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LAND DISPOSAL RESTRICTION (LDR) WASTE MANAGEMENT STRATEGY AT ROCKY FLATS

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ABSTRACT. The Rocky Flats Plant (RFP) is a government-owned, contractor-operated facility which is a part of the nationwide Department of Energy (DOE) nuclear weapons production complex. Rocky Flats has accumulated (and will continue to generate) a substantial quantity of mixed waste subject to regulation under the land disposal restrictions (LDR) of the Resource Conservation and Recovery Act (RCRA). These waste streams include low level mixed waste and transuranic mixed waste which are LDR primarily due to solvent and heavy metal contamination. DOE and EPA have entered into a Federal Facility Compliance Agreement (FFCA) which requires actions to be taken to ensure the accurate identification, safe storage and minimization of LDR mixed wastes prior to their ultimate treatment and/or disposal. As required by the FFCA , DOE has prepared a Comprehensive Treatment and Management Plan (CTMP) which describes the strategy and commitments for bringing LDR wastes at RFP into compliance with applicable regulations. This strategy includes waste characterization and reclassification, utilization of existing commercial and DOE treatment capacity, as well as, the development and implementation of treatment systems (and other management systems) for the purpose of achieving LDR regulatory compliance and ultimate waste disposal. This paper will give an overview of this strategy including a description of the major waste streams being addressed, the regulatory drivers, and plans and status of ongoing treatment systems technology development and implementation efforts.

Some of the ongoing activities include: a demonstration of microwave solidification technology; polymer solidification development; supercritical CO_2 extraction; investigation of "non-thermal" treatment technologies for combustible waste; and mixed waste incineration development. Some of the "low tech" approaches for dealing with LDR waste at RFP include improved grouting/cementation, and waste characterization with the objective of determining if the waste is, in fact, LDR. The overall approach to RFP's LDR waste problem is to develop waste management and treatment/handling systems which combine "high" and "low tech" solutions and to balance such factors as waste minimization, secondary waste stream generation, final waste form integrity, cost, risk, regulatory issues, and public acceptability in making decisions as to the most appropriate method(s) for achieving compliance.

INTRODUCTION

The Rocky Flats Plant (RFP), located approximately 16 miles northwest of Denver, Colorado, has accumulated (and will continue to generate) a substantial quantity of mixed waste subject to regulation under the land disposal restrictions (LDR) of the Resource Conservation and Recovery Act (RCRA). These waste streams include approximately 56,000 m^3 of low level mixed (LLM) waste and 750 m^3 of transuranic mixed (TRM) waste which are LDR primarily due to solvent (i.e. carbon tetrachloride and trichloroethane) and

heavy metal (i.e. cadmium, chromium, and lead) contamination. Currently RFP's mixed wastes are segregated into 40 LLM waste forms and 22 TRM waste forms. By far the largest fraction of this waste is waste water and sludges associated with the cleanup of RFP solar evaporation ponds. The second largest fraction of this waste includes newly generated and backlog nitrate salt waste. Other major categories of mixed waste include waste water treatment precipation sludge waste, miscellaneous solid combustibles such as filters, paper, rags, coveralls, plastics, etc., contaminated machining, lubricating, and hydraulic oils, roaster oxide, leaded gloves, metal and lead waste, etc. A breakdown of these major waste categories is shown in Figs. 1 and 2.

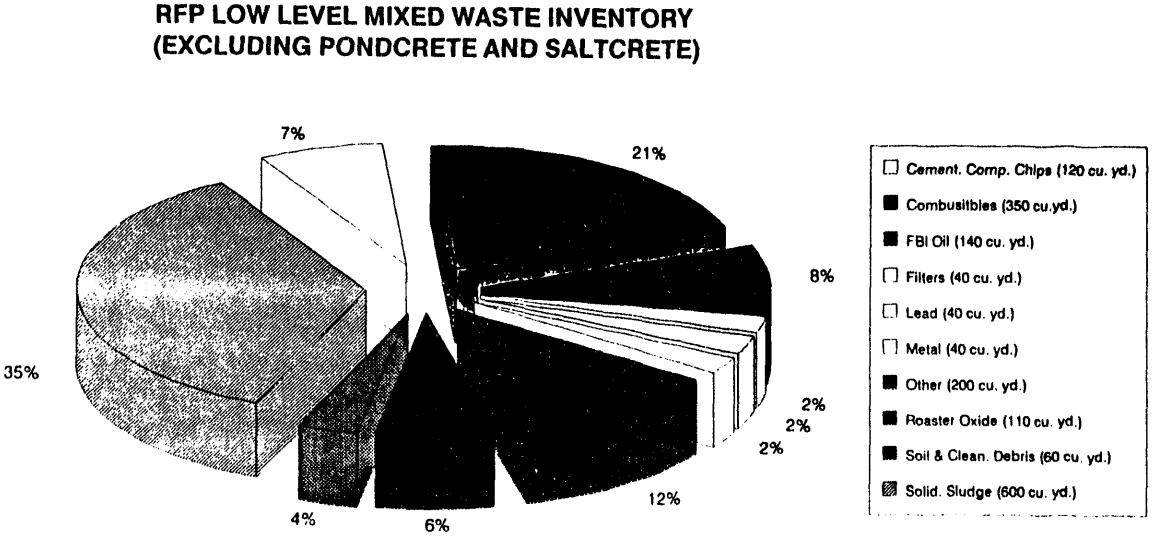

Figure 1. RFP low-level mixed waste inventory (excluding pondcrete and saltcrete).

In 1989 the Department of Energy (DOE) informed the Environmental Protection Agency (EPA) that RFP was accumulating/storing LDR waste in violation of Resource Conservation and Recovery Act (RCRA) regulations. This lead to a Federal Facility Compliance Agreement (FFCA I) between DOE, EPA and the Colorado Department of Health. FFCA I, signed in September 1989, required DOE to take actions to ensure the accurate identification, safe storage, and minimization of LDR wastes prior to ultimate treatment and/or disposal. A follow-on agreement commonly referred to as FFCA II was signed in May 1991. This agreement also requires DOE to take the necessary steps to address and resolve the LDR issue at RFP. As a requirement of FFCA II DOE has prepared a Comprehensive Treatment and Management Plan (CTMP) which outlines the overall strategy and commitments for bringing LDR waste at RFP into compliance with the applicable regulations. Progress toward achieving compliance and an update of the strategy is reported in an Annual LDR Progress Report. This strategy includes the development and implementation of treatment and management systems required to achieve LDR compliance.

REGULATORY DRIVERS

Radioactive mixed wastes are wastes that contain a radioactive component subject to regulation under the Atomic Energy Act (AEA) and a hazardous waste component subject to regulation under the Resource

Conservation and Recovery Act (RCRA). Mixed wastes are currently generated, treated and stored at RFP and are subject to federal and state statutory and regulatory requirements. DOE has responsibility for ensuring the requirements of the AEA are met, and EPA Region VIII and the State of Colorado, via the Colorado Department of Health (CDH), have the responsibility for ensuring the requirements of RCRA are met at RFP.

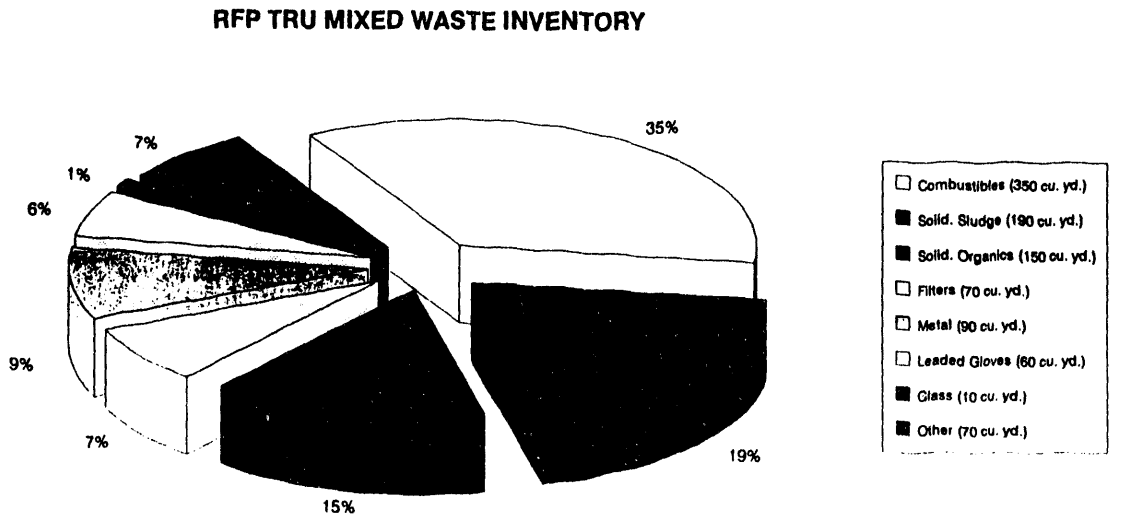

Figure 2. RFP TRU mixed waste inventory.

The U.S. Environmental Protection Agency (EPA) defines a hazardous waste as any solid waste that is either listed by regulation as a hazardous waste or possesses one of the four characteristics (ignitability, corrosivity, reactivity, and toxicity) that make the waste a hazardous waste (1). The U.S. The State of Colorado, via the Colorado Department of Health, has received authority from EPA to administer RCRA, and many portions of the Hazardous and Solid Waste Amendments (HSWA), in Colorado, and has adopted the same definition of hazardous waste in the Colorado Code of Regulations (2). For those wastes that are defined as hazardous, there are a variety of standards and regulations that must be met in order to protect the safety of the public, the worker, and the environment from potential waste mismanagement. One such set of standards is identified in Title 40 of the Code of Federal Regulations (40 CFR 268) and in the Colorado Hazardous Waste Regulations (6 CCR 1007-3, Part 268) as the Land Disposal Restriction (LDR) regulations. The LDR regulations prohibit indefinite storage of LDR wastes, unless such storage is for the purpose of accumulating sufficient quantities to effect proper treatment, disposal or recovery.

As a result of the promulgation of the LDR regulations, and due to the unique nature of mixed wastes, DOE notified EPA in 1989 that the RFP was storing mixed waste that were subject to the LDR regulations, and that such storage might not be solely for the purpose of accumulating sufficient quantities necessary to

facilitate proper recovery, treatment, or disposal, since the methods and technologies for doing so did not exist. Following this notification, DOE, EPA, and CDH entered into a Federal Facility Compliance Agreement to establish a mechanism for DOE to achieve compliance with the storage prohibition language.

In addition to current Federal and State regulations regarding the land disposal of hazardous and mixed wastes, there are other regulations and requirements that must be met in order to effectively (and legally) develop treatment and management systems for resolving the mixed waste problems associated with mixed wastes. The major regulatory drivers that must be considered in developing a management and implementation plan for compliance with the LDR regulations can be grouped into three main categories: (1) Federal and State statutes, regulations, and requirements; (2) treatment and disposal site waste acceptance criteria; and, (3) local facility policies and procedures. A condensed list of these drivers is provided below, with discussion following on those that have the biggest current impact.

CONGRESSIONAL ACTIONS

Resource Conservation and Recovery Act (RCRA)
Hazardous and Solid Waste Amendments (HSWA)
Federal Facility Compliance Act
National Environmental Policy Act

FEDERAL REQUIREMENTS

Title 40 of the Code of Federal Regulations
Title 49 of the Code of Federal Regulations
Federal Facility Compliance Agreement - Docket No. RCRA(3008) VIII-89-25
DOE Order 5820.2A - Radioactive Waste Management
DOE Order 5400.3 - Hazardous and radioactive Mixed Waste Program
DOE Order 4700.1 - Project Management System
DOE Order 5700.6C - Quality Assurance
DOE Order 5480.19 - Conduct of Operations
DOE Order 1540.1 - Material Transportation and Traffic Management
DOE Order 1540.2 - Hazardous Material Packaging for Transportation
DOE Order 5480.11 - Radiation Protection for Occupational Workers
DOE Order 5480.1B - Environment, Safety, and Health Program for DOE Operations
DOE Order 6430.1A - General Design Criteria

STATE REQUIREMENTS

Colorado Hazardous Waste Act
Colorado Hazardous Waste Regulations
Rocky Flats Plant RCRA Permit No. 91-09-30-01

TREATMENT/DISPOSAL SITE WASTE ACCEPTANCE CRITERIA (WAC)

NVO-325 - Nevada Test Site Waste Acceptance Criteria
WIPP-DOE-069 - Waste Acceptance Criteria for WIPP
DSSI WAC
SEG WAC

RFP PLANT POLICIES/PROCEDURES

4-5 Control of Employee and Environmental Exposures to As Low as Reasonably Achievable (ALARA)
6-6 Management of Hazardous and Mixed Waste Material
6-9 Radioactive Waste Management
9-10 Plant Configuration Change Control Program
9-12 National Environmental Policy Act

LAND DISPOSAL RESTRICTION REGULATIONS

In 1976 Congress passed Public Law 94-580, otherwise referred to as the Resource Conservation and Recovery Act of 1976 (RCRA). RCRA has since been amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA). Under HSWA, the EPA was tasked with promulgation of regulations to prohibit the land disposal of untreated hazardous waste. In 1986, EPA initiated its promulgation of regulations regarding land disposal of hazardous waste. This rule making process has continued through to the present and the most important facets of this process to RFP are summarized below:

May 1986 -	all hazardous wastes regulated as LDR wastes (except for solvent and/or dioxin contaminated wastes and "California List" wastes) were divided into three categories. These three categories are now commonly referred to as the "first third", "second third", and "third third" wastes.
November 1986 -	EPA issued LDR regulations regarding the prohibition from land disposal of wastes containing spent solvents and/or dioxins.
July 1987 -	EPA promulgated LDR regulations regarding the prohibition from land disposal of so-called "California List" wastes, where the "California List" waste category generally includes liquid hazardous wastes containing halogenated organic compounds, wastes with a pH less than 2, and liquid hazardous wastes containing PCBs.
August 1988 -	EPA promulgated LDR regulations for the "first third" wastes, where the "first third" category included specific F and K listed wastes.
June 1989 -	EPA promulgated LDR regulations for the "second third" wastes, where the "second third" category included additional F and K listed wastes, as well as a variety of P and U listed wastes.
June 1990 (eff. May 8, 1990) -	EPA promulgated final rules for "third third" wastes (which included all remaining listed and characteristic wastes not previously addressed under previous rule makings, but excluding all "newly identified" wastes). In addition, EPA also granted a two year National Capacity Variance for all "third thirds" mixed wastes due to a recognized lack of mixed waste treatment and disposal capacity on a nationwide basis.
August 1992 -	In order to more effectively implement the LDR regulations for debris type wastes, the EPA published final rules establishing treatment standards for hazardous debris (referred to as the "Debris Rule").

The basic premise behind the rule makings listed above was to develop specific treatment standards for the treatment of hazardous waste such that it could be effectively and responsibly disposed of, while at the same time being protective of human health and safety, as well as preserving the environment. As a result, EPA developed two basic sets of criteria for determining when and if a hazardous waste could be land disposed.

First, concentration based treatment standards were developed based on actual, or expected, hazardous constituent migration concentration data that might result from a typical disposal scenario. In other words, based on interactions of a waste with its disposal environment, hazardous constituents are expected to migrate from a hazardous waste and enter the environment. The concentration based treatment standards were then developed with this in mind, resulting in a set of numerical standards whereby wastes that did not exceed these numerical standards could be disposed in a hazardous waste land disposal facility, while wastes that did exceed the standards would have to be treated prior to land disposal.

The second set of treatment standards consists of a specified set of technologies that must be utilized prior to land disposal of certain wastes. This set is commonly referred to as "treatment-based" standards. Different from the "concentration based" treatment standards, "treatment based" standards actually require the application of a specific technology to treat the waste, regardless of the concentration of hazardous constituents in the matrix. One example is the requirement to treat PCB wastes contaminated with listed solvents utilizing incineration.

DEBRIS RULE

In August 1992, EPA promulgated a final rule called "Land Disposal Restrictions for Newly Listed Wastes and Hazardous Debris" (3) or subsequently referred to as the "Debris Rule". Among other things, the final rule promulgated treatment standards for debris contaminated with listed hazardous waste or debris that exhibits certain hazardous waste characteristics. In this rule, EPA defined debris as any solid material exceeding 60 mm particle size that is also a manufactured object, or plant or animal matter, or natural geologic material except for any material for which specific treatment standards had previously been promulgated. Examples of debris that were highlighted in the rule include glass, concrete, bricks, non-intact containers, tanks, pipes, scrap metal, rock, paper, plastic and rubber.

Recognizing the difficulty associated with characterizing most of these debris wastes, and in keeping with their philosophy of moving more toward performance based treatment standards rather than concentration based treatment standards, EPA developed the treatment standards for hazardous debris in the form of technology based treatment requirements. In all, EPA recommended 17 different extraction, destruction, and immobilization technologies (or technology categories) that could be used for treatment of hazardous debris. These technologies (and categories) are listed below:

PHYSICAL EXTRACTION
1) abrasive blasting
2) scarfing, grinding, planing
3) spalling
4) vibratory finishing
5) high pressure steam/water removal

THERMAL EXTRACTION
1) high temperature metals recovery
2) thermal desorption

CHEMICAL EXTRACTION
1) water wash/spray
2) liquid phase solvent extraction
3) vapor phase solvent extraction

CHEMICAL DESTRUCTION
1) chemical oxidation
2) chemical reduction

BIOLOGICAL DESTRUCTION
1) biodegradation

THERMAL DESTRUCTION
1) incineration

IMMOBILIZATION
1) macroencapsulation
2) microencapsulation
3) sealing

It is obvious that each technology listed above is not appropriate for each possible debris waste that could be generated. In order to prevent the possibility of utilization of an inappropriate technology, EPA also provided certain contaminant restrictions and certain performance standard restrictions, that limit the applicability of any particular technology to those debris waste forms for which it would be most effective.

Although EPA indicated in the rule that existing concentration based treatment standards could still be pursued (i.e., the hazardous debris standards do not have to be followed simply because a hazardous debris exists), there are significant advantages for a generator of hazardous debris to utilize the technology specific standards, especially when management of mixed wastes is at issue. First, it provides a mechanism for dealing with non-homogeneous wastes by eliminating most of the up-front physical characterization requirements. The waste must still be characterized, however, the rigor applied to this characterization is much less demanding. Second, the rule provides for post treatment disposal of certain debris forms in a RCRA Subtitle D landfill. In other words, once treatment has been accomplished, debris wastes that have been treated via an extraction or destruction technology are no longer considered to contain the hazardous waste, and therefore, are considered non-hazardous. In the case of treatment utilizing immobilization technologies, the treated waste must still be managed as a hazardous waste because immobilization does not remove the hazardous contaminant, it only stabilizes it.

Based on the above information, the "Debris Rule" has the potential to impact the overall LDR compliance approach for a variety of waste streams generated and stored at RFP. Fortunately, through the development of the CTMP, RFP is already pursuing development of most of the recommended technologies, and in fact, many of the debris technologies are actually the primary treatment method proposed in the CTMP [e.g., polymer encapsulation (immobilization) for leaded gloves].

A preliminary assessment of the applicability of the "Debris Rule" to RFP wastes in storage was conducted. Based on this assessment, the following wastes have the potential to fit into the category of hazardous debris:

1) combustibles
2) cutoff sludge (possible)
3) filters and filter media
4) glass
5) glovebox parts
6) ground glass (possible)
7) heavy metal
8) insulation
9) lead
10) leaded gloves
11) metal
12) PCB solids
13) soil and cleanup debris (possible)

The full significance of the impact this rule may have at RFP is still being evaluated, however, certain preliminary conclusions can be drawn.

First, inherently hazardous debris (i.e., debris that is inherently hazardous as a result of its chemical construct or based on its fabrication) such as glass (i.e., leaded glass), glovebox parts (i.e., lead shielding), ground glass, heavy metal, lead, leaded gloves, and metal, must be treated utilizing an immobilization technology as a result of specific requirements in the "Debris Rule". The CTMP currently outlines the development of a treatment system utilizing macroencapsulation to treat these wastes. In this case the resultant treated waste must still be managed as a hazardous waste.

Second, other debris wastes including combustibles, filters, insulation, and soil and cleanup debris could be treated utilizing an extraction technology (e.g., thermal desorption) and the resultant waste could then be managed as non-hazardous. Pursuit of this debris technology results in a small deviation from the CTMP treatment system in which thermal treatment (i.e., incineration) was proposed. However, thermal desorption

technologies are being pursued as an alternative to thermal treatment in the event that it proved politically or technically unpalatable.

Third, although RFP is already pursuing most of the "Debris Rule" technologies, the order in which they are pursued (given a finite amount of funding) and the priority that is placed on developing specific technologies may need to be modified from the currently proposed compliance paths already in existence in the CTMP.

FEDERAL FACILITY COMPLIANCE ACT OF 1992

The Federal Facility Compliance Act ("The Act") was signed by President Bush on October 6, 1992. This Act, among other things, modifies Section 6001 of the Resource Conservation and Recovery Act to indicate that the United States (i.e., Federal Agencies) waives sovereign immunity for violations of RCRA, HSWA, existing permits, agreements, and compliance orders entered pursuant to RCRA. A specific provision of "The Act" recognizes that federal agencies (e.g., the Department of Energy) who manage mixed waste can not immediately comply with the storage prohibition provision contained within the LDR regulations. As such, the waiver of sovereign immunity is not effective until 1995 for violations of the LDR storage prohibition for these agencies. This extension is valid only as long as these agencies manage their mixed waste appropriately in accordance with all other applicable regulations, and as long as the additional terms of "The Act" are completed. Additional terms applicable to the Department of Energy include preparation of a National Inventory Report, a National Treatment Capacity and Technology Report, and a Plan for Developing Treatment Capacities and Technologies Report. DOE is currently pursuing the preparation of these documents, and the third submittal in particular will significantly influence the manner in which RFP achieves compliance with the LDR regulations.

STRATEGY

RFP has adopted a multiple path approach for achieving LDR compliance which is described in the CTMP and updated in the Annual LDR Progress Report. This approach is illustrated in Fig. 3 and includes two pathways for achieving compliance for TRM waste and four pathways for achieving LLM waste compliance.

TRM waste is planned for ultimate disposal at the Waste Isolation Pilot Plant (WIPP). It is assumed that WIPP will receive a no-migration variance and will be permitted to receive untreated LDR waste. Therefore, the strategy for TRM waste LDR management includes characterization to ensure the waste meets WIPP waste acceptance criteria (WAC) and shipping requirements. If WIPP WAC and shipping requirements are met, waste will be shipped to WIPP untreated (Path E). However, in some instances TRM waste will require treatment to meet WIPP WAC and/or shipping requirements (Path F). Further, in some instances it may make economic sense to treat the waste prior to shipment (e.g. volume reduction or actinide separation).

Figure 3 depicts four pathways for achieving LDR compliance for LLM waste. Path A focuses on waste characterization for "reclassification" of selected waste streams. LDR waste determinations at RFP are primarily based on process knowledge and in a few cases on limited analytical data. In the past, RFP has generally taken a conservative approach to making the LDR determination, assuming the waste was LDR if the possibility of LDR contamination existed. Currently, RFP is working closely with the regulators and shifting away from this overly conservative approach to waste classification. Through reevaluation of process knowledge and by obtaining additional analytical data when required, RFP is reevaluating some of the original LDR determinations. This has and will result in a determination that some of the waste forms are not hazardous and can be managed as straight low level waste. If it is determined that the waste has

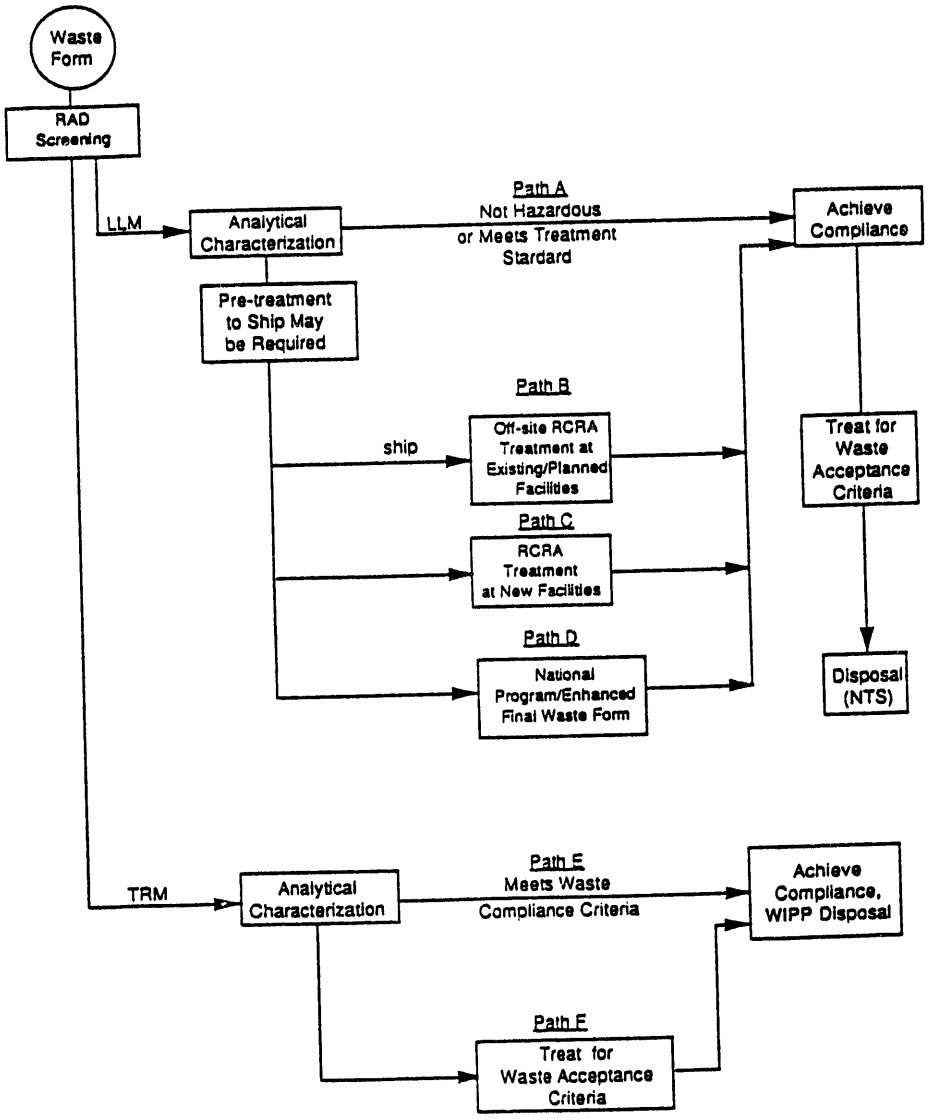

Figure 3. Multi-path approach for achieving LDR compliance.

been LDR contaminated, Path A characterization could result in a determination that the contamination is below the concentration based LDR treatment standards and no further treatment is required prior to final disposal. Further, the analytical data obtained as part of Path A will be used for LDR treatment system development if treatment is required.

Path B focuses on LDR waste treatment at existing or planned DOE or commercial treatment facilities. This path is being pursued because there is the potential for lower cost and shorter schedules by utilizing existing or planned facilities rather than building new facilities. RFP has evaluated over two hundred facilities to look for facility/waste form matches. This initial evaluation has resulted in a preliminary match at 22 DOE facilities and 4 commercial facilities. It should be pointed out that these preliminary matches do no completely consider many of the "non-technical" road blocks to off-site treatment such as permit conditions, and unwillingness of particular states to allow out of state waste treatment. RFP is currently aggressively

pursing treatment of two LDR waste forms at two commercial treatment facilities.

Path C represents the baseline path for LLM waste compliance. That is, DOE is committed to building new treatment systems under path C if management of the LLM waste can not be achieved or is impractical under the other three paths. Path C includes the development and implementation of six primary treatment. The six treatment systems are: (1) LLM Solar Pond Cleanup Treatment System; (2) LLM Solidified Bypass Sludge Treatment System; (3) LLM Building 374/774 Treatment System; (4) LLM Miscellaneous Waste Form Treatment System; (5) LLM Surface Organic Removal, Leaded Glove and Bulk Lead Treatment System; (6) LLM Solvent Contaminated Waste Treatment System.

Path D is a recognition that the mixed waste/LDR waste problem is being pursued on a national basis. When the CTMP was originally written Path D focused on waste treatment which resulted in an enhanced final waste form. However, Path D has expanded beyond the enhanced final waste form focus to incorporate the overall national mixed waste strategy which includes technology development under the Mixed Waste Integrated Program, planned technology demonstrations under the Mixed Waste Treatment Project, the National Mixed Waste Compliance Plan published in the Federal Register in December 1992, and Federal Facility Compliance Act activities.

Since the CTMP was originally written there has been a shift in emphasis in an attempt to improve schedule and cost considerations while at the same time not sacrificing risk and regulatory considerations. This change in emphasis is due in part to interaction with the regulatory community and the public. This shift in emphasis includes more emphasis on: waste characterization and reclassifications (Path A); use of commercial facilities (Path B); expedited development of existing technologies; and taking advantage of "debris rule" technologies. By shifting the emphasis away from building new treatment facilities (Path C) it is felt that RFP will be able to manage the LLM waste in a more timely and cost effective manor.

ONGOING MANAGEMENT ACTIVITIES

In addition to the actual physical development of treatment technologies identified as Path C (above), there are a variety of other management alternatives being pursued as highlighted in Paths A and B.

Program management activities are integral to the compliance effort, as the use of sound management tools and strategies assures that current year and out-year compliance efforts remain cost effective and technically efficient. The program management approach developed to date will assist in defining the framework for current (and future) decision making regarding the most appropriate, efficient, and cost effective approach for achieving compliance. The most important aspect of efficient program management is the development of a documented project plan. This project plan serves to establish a baseline for management of the overall program, lists the assumptions for program implementation, and defines the resources required to accomplish the program objectives. In addition to the project plan, a variety of other management tools have been developed to assist in program implementation and decision making including a CTMP Implementation Cost and Schedule Model, a Technology Selection Decision Document, an Issues Analysis Document, and a Risk Management Plan. The applicability of these to RFP's compliance approach are highlighted briefly below.

CTMP IMPLEMENTATION COST AND SCHEDULE MODEL

The CTMP Implementation Cost and Schedule Model ("Model") was developed in order to provide a systematic quantification of activities required to meet RFP's commitments in the FFCA and CTMP. Development of the "Model" has allowed RFP access to a management tool that provides concise information about plans, budgets, technical interrelationships between activity schedule and logic, and the ability to assess impacts for proposed and actual changes to commitments. Use of the "Model" provides for the ability to fully analyze the impact(s) of alternative compliance strategies prior to actual

implementation of a modified strategy. The model was developed utilizing typical project management techniques and concepts including development of a work breakdown structure, a schedule, resource availability and allocation tables, and a responsibility assignment matrix. Integration of these items provides the opportunity to develop extremely detailed schedules (and related costs) for options analysis.

TECHNOLOGY SELECTION DECISION DOCUMENT

A Technology Selection Decision Document (TSDD) was developed as an additional management tool for the purpose of documenting decisions made regarding the applicability (or non-applicability) of treatment technologies chosen for treating mixed waste, as well a for providing a systematic methodology for evaluating specific technologies for applicability based on a variety of factors including political, social, technical, and economic factors. The TSDD is a tool for ensuring that treatment technology decisions are defensible and traceable to rationale based on data of assessed quality. The TSDD also prevents and resolves gaps in the coverage of waste stream constituents/characteristics of concern for LDR compliance. The TSDD does not include actual technology modeling or selection. Instead, it is designed to establish a technology selection database, from which treatment systems (i.e., combinations of individual treatment technologies) are chosen to provide comprehensive treatment for all constituents/characteristics of concern. The TSDD also provides the mechanism to optimize selection of treatment systems to meet specific cost, schedule, waste volume constraints, site priorities, and economies of scale.

CTMP ISSUES ANALYSIS DOCUMENT

The CTMP Issues Analysis Document (IAD) is a document that provides an overview of the problems and issues impacting implementation of the CTMP. It provides a systematic breakdown of the issues, their causes, recommended solutions, schedules and/or milestones for resolution, anticipated funding parameters for resolution, and a relative prioritization of the issues based on DOE's Five Year Plan prioritization scheme. Issues are categorized in a effort to focus on those with similar causes and/or similar solutions. The following general categories have been established: 1) Treatment technology planning issues; 2) Technology selection issues; 3) Waste characterization issues; 4) Regulatory issues; 5) Infrastructure issues; 6) Documentation issues; and, 7) Management issues. Many of the issues outlined in the IAD are outside the control of the site (i.e., they are national issues requiring national policy decisions), thus the IAD becomes extremely important for the purpose of documenting issues and recommended solutions to the decision makers who have the potential to impact program implementation.

CTMP RISK MANAGEMENT PLAN

Risk evaluation and management is a very important necessity for a program of this magnitude, especially in light of the fact that ultimate compliance for many waste streams can only be achieved through the construction and operation of a major waste treatment system. The CTMP Risk Management Plan (RMP) encompasses both risk analysis and risk control. Risk analysis includes the identification, description, and impact modeling of all sources of uncertainty throughout the life of the project. Data worth assessment (comparison of data collection cost versus risk reduction benefit) and contingency planing are the key elements of risk control. DOE guidelines (4) require risk management and the use of a risk-based graded approach in project management. The level of project control must be commensurate with the level of risk. These project controls must ensure that management attention remains focused on project risks and that timely corrective actions are taken if required. Based on DOE guidelines, CTMP implementation activities result in moderate to high risk levels. The goal of the RMP is to design and implement program controls to reduce risk and ensure implementation success.

ONGOING PATH A ACTIVITIES

Prior to disposal, mixed wastes must be adequately characterized to ensure that the concentration of hazardous constituents does not exceed the regulatory threshold values specified in the LDR regulations. Additionally, proper characterization plays an important role in defining waste classification under RCRA and also in providing the necessary radioactive, chemical, and physical data for application of appropriate treatment required to meet LDR regulations.

Because of the difficulties associated with acquisition of analytical data on radioactive mixed wastes, characterization is usually accomplished via a thorough "process knowledge" assessment, whereby existing records and process information are evaluated to determine the chemical and physical nature of the hazardous waste. "Process knowledge" in many cases, is utilized because the actual acquisition of samples, and the laboratory analysis of these samples can not be performed in a safe manner consistent with ALARA for radioactivity contaminated wastes. As a consequence, and in the interest of compliance with the identification requirements contained in RCRA, conservative evaluations are sometimes made due to the fact that numerical data can not be obtained. As a result, certain mixed wastes are classified as being subject to regulation under RCRA (and subject to the LDR regulations) when indeed they may not actually be affected. The purpose of Path A is to obtain definitive information regarding these waste streams to conclusively demonstrate one way or the other whether they should indeed be subject to hazardous waste regulation.

In order to achieve this objective, Characterization/Sampling and Analysis Plans are being developed to obtain the needed information. All forty low level mixed waste forms have been prioritized according to a documented set of criteria for the purpose of performing the investigation in the most effective manner possible. Eleven of these waste streams have been chosen for Path A based on their high probability of being non-hazardous, or based on the matrix being amenable to sampling and analysis. Two characterization plans have already been drafted, and RFP is in the process of performing internal and external review to ensure the data quality objectives have been properly stated and addressed. Upon approval, sampling and analysis will commence to obtain the required definitive information. The remainder of the waste streams will have characterization plans developed over the next 2 years in order to perform similar sampling and analysis activities.

To date, RFP has been able to eliminate three mixed waste streams from the realm of regulation due to acquisition of additional process knowledge. In addition, one mixed waste stream has been eliminated from regulation based on acquisition of actual analytical data that demonstrated that the waste did not exceed the regulatory threshold for toxic metals.

LABORATORY STATUS

As indicated above, physical sampling and analysis is complicated by the radioactive constituents associated with the waste matrix. Accepted RCRA sampling and analysis methods were not designed with radioactive components in mind, and difficulty arises at every step including sample acquisition (radiological controls prevent easy access to waste containers) and laboratory analysis (delicate analytical instruments are not designed for the abuse that occurs in glovebox operations). In spite of these difficulties, the DOE complex is making great progress in obtaining its own capacity and capability. In addition, the commercial sector has recognized a significant market deficiency in this area, and a variety of commercial firms are beginning to aggressively pursue acquisition of radioactive sample analysis capability. RFP is currently pursuing an increase in on-site laboratory capability and capacity, as well as performing audits on off-site commercial and DOE facility laboratories to utilize their capability and capacity as well.

Based on acquisition of enhanced process knowledge and analytical data, it is expected that the actual set of mixed waste streams that must be treated will decrease significantly, thus resulting in decreased long

range costs required for development of treatment systems that might not actually be necessary.

ONGOING PATH B ACTIVITIES

RFP continues to evaluate the availability of off-site commercial and DOE facilities for treatment of mixed waste and is currently pursuing the utilization of commercial facilities for the processing of low level mixed wastes. Significant progress includes the identification of candidate waste forms for off-site disposal and the evaluation and investigation of off-site facilities. RFP will also continue to monitor the technical, political, and legal feasibility of treating mixed wastes at commercial treatment facilities. As commercial facilities become available and are approved for treatment of RFP wastes, RFP will request that one or more of the baseline treatment systems (a.k.a. Path C) be replaced with commercial treatment (as appropriate). Again, as with Path A above, the objective is to achieve compliance in the most effective, efficient manner possible. Utilization of existing treatment capacity outside of RFP will eliminate the need to construct and operate completely new treatment systems.

A comprehensive assessment of potential off-site treatment facilities was conducted (and continues to be updated) in which on-site facility assessments, interviews with facility engineers, management and operators, acquisition of facility documentation, permits,, etc. were utilized to ascertain the feasibility of off-site treatments. In addition to facility specific investigation, federal and state requirements concerning treatment, storage, and disposal were identified for the purpose of identifying issues associated with treatment of out of state waste (e.g., certain states require special radioactive materials transportation permits or licenses). In all, 24 DOE facilities were consulted to determine applicability of their existing and planned facilities for treatment of RFP wastes. At these 24 facilities, 207 treatment systems were assessed. Of these 207 treatment systems, 22 systems located at 9 different DOE sites were determined to have some applicability to RFP mixed wastes In most cases, there are significant interstate issues involved as well as the fact that most existing facilities are at capacity, and will remain at capacity until well into the next century. This probably limits the actual availability of these systems for RFP waste, however, RFP is continuing to monitor progress.

Additionally, on the commercial side, there are currently only a handful of facilities that have the proper radioactive materials handling licenses. Of these, four commercial sites have been identified as having the potential to manage RFP mixed wastes. Negotiations with these facilities will commence once the political and economic issues have been resolved.

ONGOING PATH C ACTIVITIES

Path C development programs are designed to support six different waste treatment systems. These activities are aimed at three different technical areas needed to support specific unit operations. The three technical areas are solidification, destruction of organic materials and volatilization of hazardous solvents contained within a waste matrix. Several different technologies are being evaluated in parallel in order to develop acceptable solutions for the three technical areas and all six Path C waste treatment systems. With only one exception, microwave melting, the technologies being developed are adaptations of development work being performed at other facilities and/or existing processes.

Solidification-Cementation

The Rocky Flats cementation development program is aimed at developing cement formulations that work with specific waste forms and that can be processed in existing or planned equipment. Even though grouting/cementation is well understood, it is necessary to tailor formulations to account for waste stream chemistry variations so that regulatory characterization requirements such as the Toxicity Characterization

Leaching Procedure (TCLP), transportation requirements, and the final disposal site Waste Acceptance Criteria (WAC) are met.

Cementation development focusing on nitrate salts produced by the Building 374 Evaporation system is one example of ongoing RFP solidification development. Current production of grouted nitrate salts is in the process of being recertified for disposal at the Nevada Test Site (NTS). In the past, batches of grouted nitrate salts, ('saltcrete') have been disposed of at NTS and met all waste acceptance requirements in place at the time of shipment. However, more recently, RFP was unable to ship the saltcrete to NTS. The saltcrete was stored outside at Rocky Flats awaiting shipment during which time the waste experienced a number of freeze-thaw cycles causing waste form deterioration in some instances. Current development activities are directed at preventing future degradation. Other wastes, such as waste water treatment precipitation sludges, ash and debris are additional targets of cementation development.

Solidification-Polymer Encepsulation

Because of deterioration problems and relatively poor waste loading, cementation is often not the most cost effective or "best" technical solution available for a specific waste form. Polymer encapsulation is being developed to address shortfalls of cementation. In either a microencapsulation or a macroencapsulation form, polymer processes can safely hold more than two to three times the waste when compared to a grouting/cementation process. Additionally, for targeted wastes, polymer encapsulation produces a more durable and acceptable waste form. Polymer is also ideally suited for many possible "Debris Rule" applications because the debris can be contained without resorting to thermal and chemical reaction.

Microencapsulation using extruded low density polyethylene has been tested in Japan and other countries. (See Fig. 4.) Brookhaven National Laboratory is assisting Rocky Flats and other DOE facilities in adapting this process to specific waste forms. The primary target waste at Rocky Flats is the nitrate salts from the Building 374 evaporator system, the same waste form that is presently going into 'saltcrete'. The nitrate salts are currently being dried using a spray drier; however, the morphology of the spray dried salt has been shown to be incompatible with the low density polyethylene extrusion process. Tests are being performed with candidate drying systems to assure that they will be compatible with the polymer process. Other waste forms targeted for polymer processing include precipitation sludges, ash and glovebox gloves. Initial development indicates that low density polyethylene microencapsulation will have two times the waste loading of 'saltcrete' and meet all the RCRA-LDR, DOT and NTS waste acceptance criteria. The reduction in waste volume more than makes up for the cost of the low density polyethylene and the process equipment. Additionally, low density polyethylene extrusion can be used to macroencapsulate debris. This process has the advantage of avoiding the use of hazardous chemicals employed in many of the commercial processes, which employ thermosetting plastics. Extruded LDP is potentially cheaper and safer than these hardener resin based processes.

Cold bench scale low density polyethylene co-extrusion tests are under way and preliminary TCLP results are available. A pilot system is currently being prepared for treatment of plutonium contaminated wastes. Commercial systems are being evaluated for possible use for debris and other waste forms. Selected LLM polymer encapsulated wasted forms will be produced by 1994.

Solidification-Microwave Melting

Microwave Melting is the only waste process that was developed at Rocky Flats, even though it is based on early work performed in Japan. The process is designed to use microwave energy generated outside a glovebox environment to melt waste within a glovebox. The container used to hold the waste is a standard thirty gallon stainless steel drum which is discarded with the waste. Figure 5 shows a schematic of the microwave process. Powdered or pelletized waste is continuously fed into the drum as microwave energy

is applied. Only the top one to five centimeters of material are molten at any one time.

The microwave melter is ideal for vitrifying small quantities of waste that already contains glass forming elements and/or is too radioactivity contaminated to use cementation or polymer encapsulation. Microwave melting has a higher waste loading than grouting and, for some wastes, than polymer encapsulation. As compared to other vitrification processes microwave melting is inexpensive and space efficient. Since only a small amount of material is molten at any given time and there are no refractories used and the system can be started and stopped almost instantaneously. This fast start/stop capability is a great operational and safety advantage in a glovebox environment.

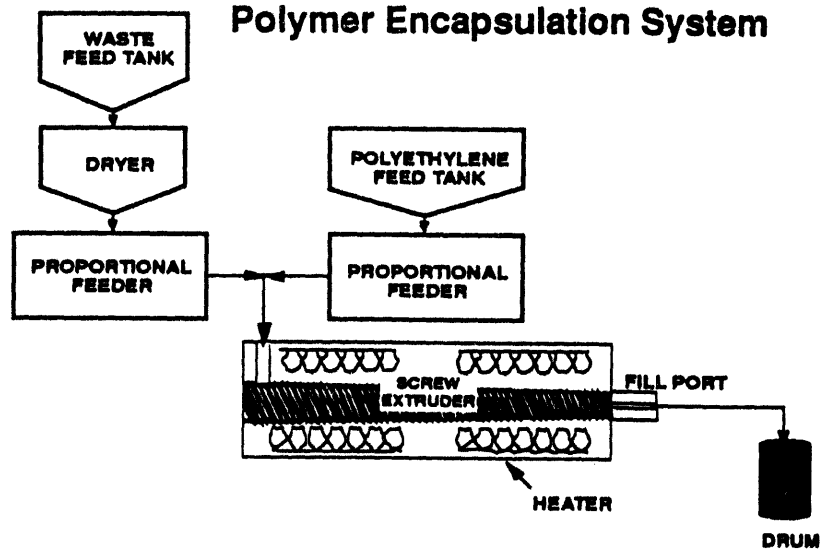

Figure 4. Polymer encapsulation system.

The microwave melting project was started in 1985. Since that time hot and cold laboratory scale, 6 kW, systems have been used to generate waste form processing data. A 30 kW pilot scale system was used to demonstrate full scale feasibility on surrogate waste. A 50 kW pilot/production scale system was developed, using the lessons learned on the prior systems. This system is currently being used to generate design data on surrogate wastes.

The microwave melter is currently targeted at processing precipitation sludges produced in Buildings 374 and 774. These sludges already contain silica in the form of diatomite, which is used as a filter media. Little or no additional 'frit' is needed in order to produce a quality vitreous-to-crystalline waste form. The Microwave is also a candidate process for incinerator ash and other sludges.

Recently, Rocky Flats has been confronted with the need to process residue materials that were previously recycled for their plutonium content. Because of glovebox and criticality restraints, the 6 kW bench scale microwave melting systems might become the 'production scale' systems to process these materials. These residues are too radioactive to process as grout or polymer, so existing microwave melting systems may be an ideal means of quickly and inexpensively converting them into a vitreous waste form.

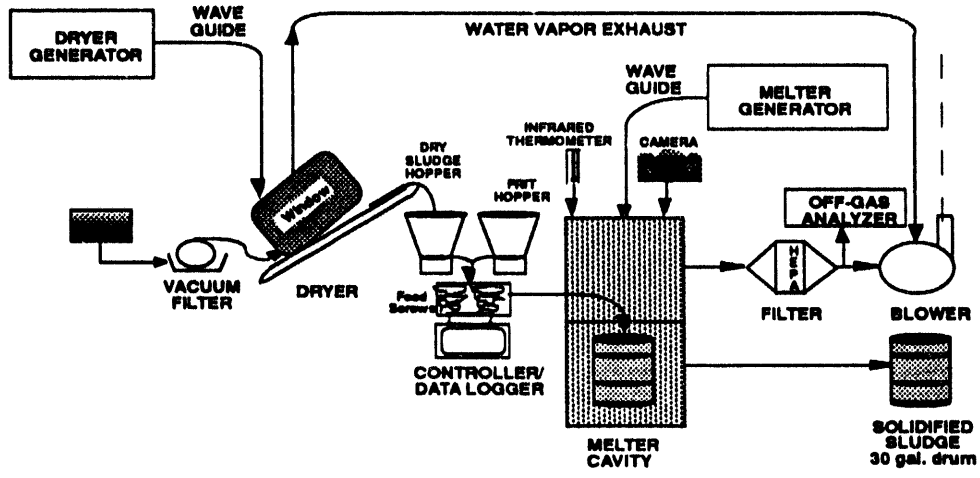

Figure 5. Microwave melter.

Organic Destruction-Fluidized Bed Unit (FBU)

Based on technical considerations alone the "best" currently available means of destroying organic wastes is incineration. Incineration is a proven method of reducing the volume to destroy the organic contamination of combustible mixed wastes. Additionally, incineration is applicable to almost all organic waste forms, liquids, solids and solids mixed with nonincinerable materials.

Fluidized bed technology was chosen for processing Rocky Flats combustible wastes in the late 1970's. Fluidized bed incineration is well suited for plutonium containing wastes. Figure 6 shows a schematic of the FBU process. The catalyzed bed material contains sodium carbonate, which neutralizes the acidic gases as they are produced. The low operating temperatures of the FBU, afforded by the catalyst, allow the primary reaction vessel to be made of metallic materials without refractories. Refractory materials are potential repositories of plutonium compounds and consequently must be routinely replaced in order to stay in compliance with criticality safety requirements. The in-situ neutralization of acid gases allows the use of a dry off-gas treatment train, which reduces the amount of secondary waste generated.

Pilot scale units were tested in the mid 1970's and a full scale pilot unit was used to process over 20,000 lb. of material by the mid 1980's. Small fires and negative public opinion forced Rocky Flats to abandon the pilot unit. However, the viability of the technology was well established and it is still considered an optimum solution for Rocky Flats combustible wastes.

The current effort is aimed at confirming that fluidized bed processing is compatible with new regulations and correcting flow problems experienced with the old units. Additionally, a great deal of emphasis is being placed on performing all work under the spotlight of the public, EPA and the Colorado Department of Health. This 'open house' development is required in order to change public perception sufficiently to have fluidized bed incineration accepted in Colorado or other locations.

Organic Destruction-Alternatives to Incineration

In order to address public and political realities associated with incineration and to demonstrate good faith with the public and regulatory community, alternatives to incineration are being investigated. Rocky Flats developed a strategy to examine a spectrum of processes that include mild to aggressive, and cold to hot (i.e. thermal) processes to oxidize organic waste materials. All of the processes are being developed outside of Rocky Flats by commercial and/or other DOE facilities. The objective of this effort is to select processes that can be used to treat liquid and solid combustible wastes present at Rocky Flats. The optimum

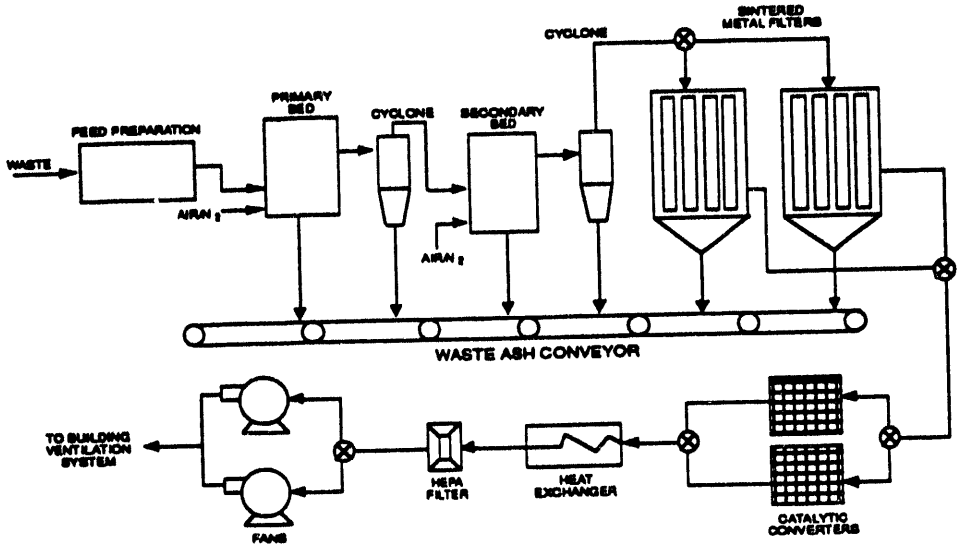

Figure 6. Rocky Flat's fluidized bed process.

selection(s) will be the minimum number of systems that can economically process all the wastes. Note; application of the recently implemented Debris Rule might reduce the amount and number of wastes that will be treated by incineration and alternatives.

The least aggressive candidate technology being evaluated is biological destruction. The primary development work is being performed under contract to Los Alamos National Lab (LANL) and the University of Colorado. Biodegradation is not applicable to polymeric solid wastes except as a surface decontamination technique; however, it has been demonstrated to be effective in processing contaminated cutting oils, which are primarily machining lubricants (Fig. 7).

Mediated Electrochemical Oxidation, MEO, utilizes an oxidizing ionic species (Ag^{++}, Co^{+++}), produced electrochemically, to react with organic wastes (Fig. 8). Similar systems are in industrial use in Europe to strip organic solvents and transuranic contamination from waste in addition to oxidizing organic materials. Again this technology probably is not aggressive enough to practically oxidize polymeric wastes. However, it has been demonstrated as an oxidizing treatment for organic solvents and cellulosic materials.

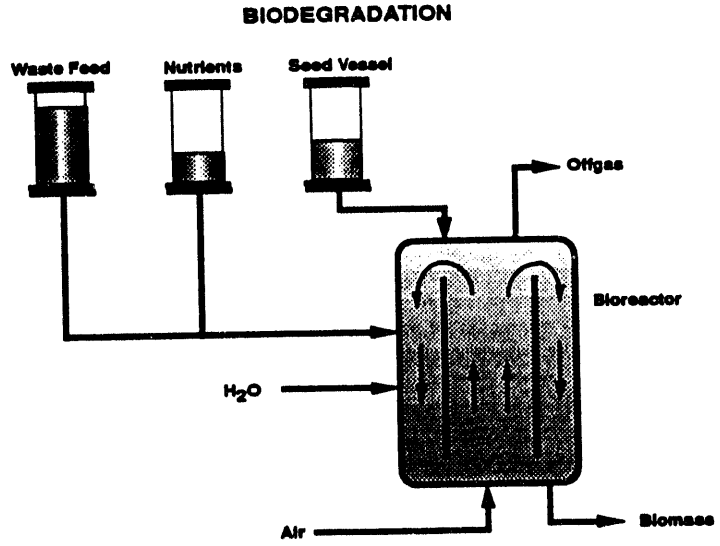

Figure 7. Biodegradation

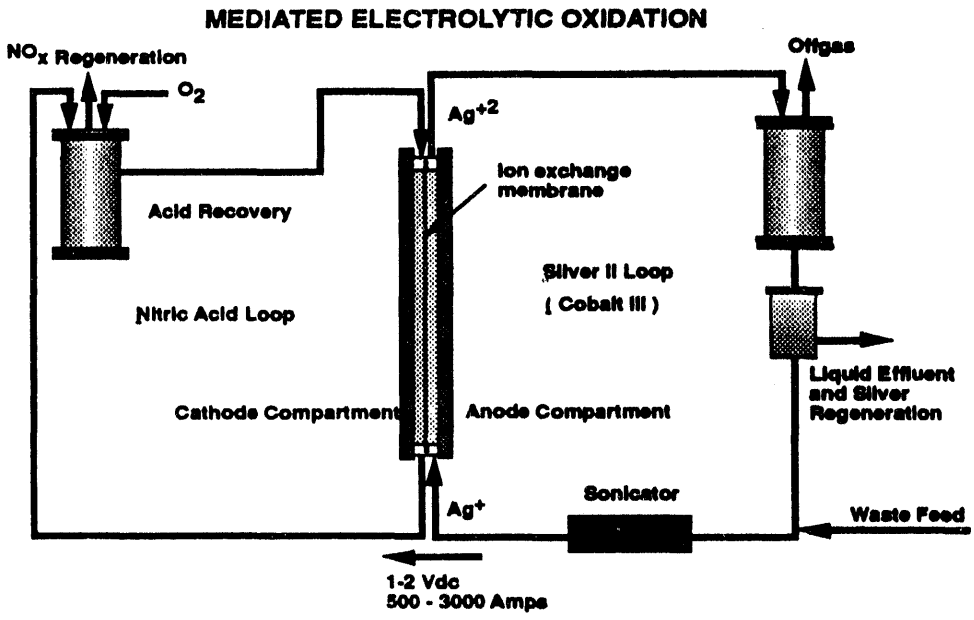

Figure 8. Mediated electrolytic oxidation.

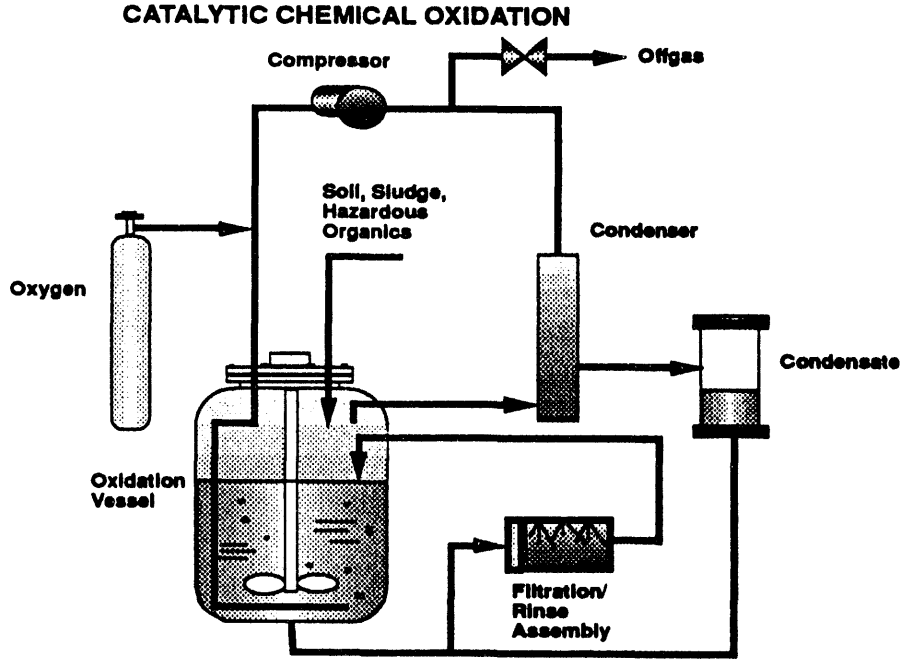

Figure 9. Catalytic chemical oxidation.

Catalytic chemical oxidization, CCO, is being developed by Delphi Research Inc. (Fig. 9). This process is aggressive enough to oxidize polymers and other combustible wastes. Consequently, it appears to be the best alternative to incineration technology identified so far. However, systems design for CCO systems is in its infancy. There are major concerns with corrosion and materials of construction.

The most aggressive candidate system for liquid waste appears to be the silent discharge plasma/packed bed reactor system, SDP, being developed by LANL (Fig. 10). This system uses a stationary packed catalyst bed, similar to that used in the FBU. Any residual hazardous constituents are reacted in the ozone forming region of micro discharge plasma cell. The SDP technology can also be used to process off gas from volatilization systems and incinerators. However, the SDP system is a thermal system and might be as difficult to permit as an incinerator.

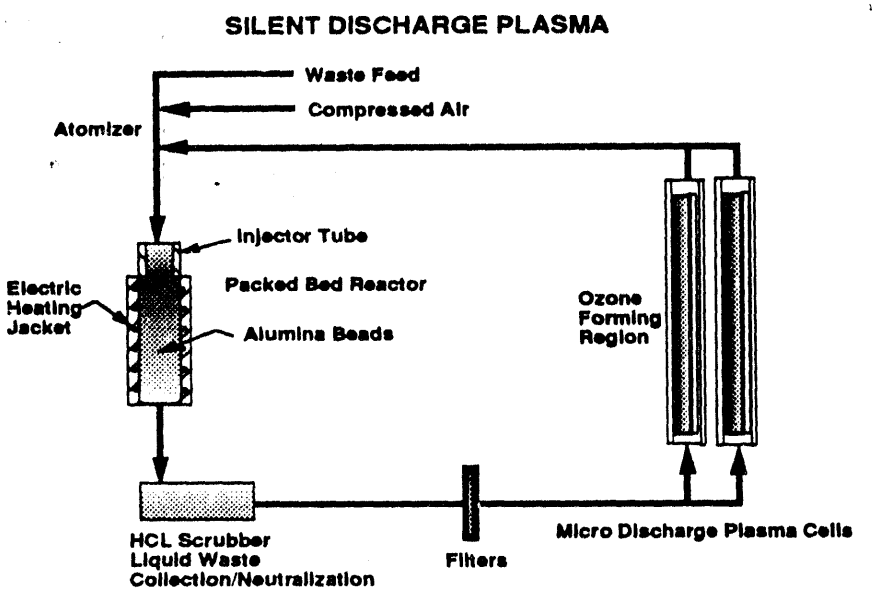

Figure 10. Silent discharge plasma.

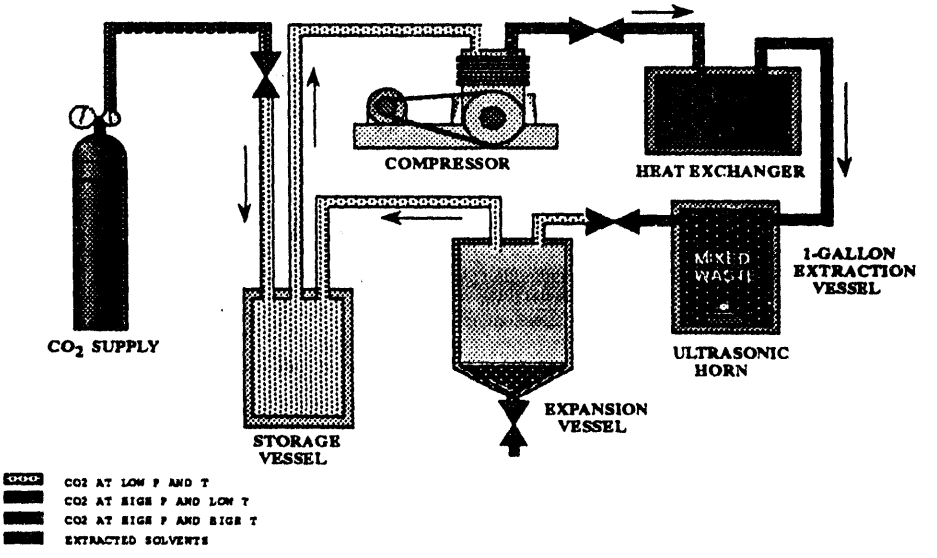

Figure 11. Supercritical carbon dioxide extraction.

Volatilization

Many volatilization technologies are commercially available. These include nitrogen, steam and vacuum stripping. The volatilization processes can be use to remove hazardous solvents from waste that can then become LDR compliant and/or make the material a candidate for debris treatment.

In addition to the more conventional volatilization technologies, Rocky Flats has technical expertise with supercritical carbon dioxide extraction (SCCDE) (Fig. 11). This process takes advantage of the solvent properties of supercritical carbon dioxide. The solvency can be controlled by adjusting the temperature and pressure of the process. The carbon dioxide can be trapped and separated from the hazardous solvents in the expansion vessel, so that it can be recycled. SCCDE development is being pursued to the extent that it can be compared to commercially available volatilization processes, after which a process or processes can be selected.

CONCLUSIONS

The basic purpose of the LDR regulations is to allow for the disposal of hazardous waste and at the same time provide for protection of human health and the environment throughout the process. In short, the LDR regulations have been established to ensure that the toxicity of the hazardous constituents intended for disposal are decreased in order to prevent short and long term health effects. In addition, the LDR regulations were established on the basis of ensuring that there is a reasonable degree of certainty that hazardous constituent migration is prevented for as long as the waste remains hazardous. Compliance with the LDR regulations is particularly difficult for mixed waste due to the added complications associated with the radioactive component of the waste. By adopting a flexible multiple path approach to RFP's LDR waste problem it is possible to achieve compliance in a cost effective and timely manor. RFP's overall strategy is to develop and implement management and treatment systems which combine "high" and "low tech" solutions while balancing technical and non technical issues in selecting the most appropriate method(s) for achieving compliance.

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2. Colorado Department of Health, Colorado Hazardous Waste Commission, Identification and Listing of Hazardous Waste, 6CCR1007-3, Part 261 (January 1993).
3. EPA (U.S. Environmental Protection Agency), Land Disposal Restrictions for Newly-Listed Wastes and Hazardous Debris, Fed. Reg. 57:37194 (1992).
4. DOE (U.S. Department of Energy), Project Management System, Project Control System Guidelines Implementation Reference Manual, DOE Order 4700.1, DOE Notice 4700.5.

TREATMENT OF MIXED F006 CONTAMINATED MATERIAL TO MEET THE NEW EPA DEBRIS RULE AT THE SRS

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ABSTRACT. The Westinghouse Savannah River Company (WSRC), as the operating contractor for the Department of Energy at the Savannah River Site (SRS), has demonstrated a procedure to clean mixed (radioactive/hazardous) wastes to meet the criteria in the recently promulgated Land Disposal Restrictions "debris" rule. The waste was equipment (steel piping, transfer pumps, valves) which had been used in an industrial wastewater treatment facility to transfer listed F006 wastewater treatment plating line sludges to a Resource Conservation and Recovery Act (RCRA) storage tank complex. When the equipment needed to be replaced/repaired, it was concluded that the resulting debris would have to be managed as a mixed waste, due to the fact that the solid waste "contained" the listed hazardous waste and a radioactive constituent.

WSRC gained concurrence from the Environmental Protection Agency, Region IV, that the equipment could be flushed in place as an integral part of a wastewater treatment facility, prior to dismantlement and replacement. If the piping and pump parts met the "clean debris surface" definition (in the debris rule) after removal, it could be discarded as a non-hazardous waste. If however, it did not meet the clean surface criteria at that stage, it was agreed that the equipment to be discarded could be treated in an accumulation container under the RCRA 40 CRF 262.34 regulations - without RCRA treatment permitting requirements. After additional scrubbing and cleaning, the equipment was discarded as a non-hazardous low-level radioactive waste to the SRS Solid Waste Disposal Facility.

INTRODUCTION

The M-Area Liquid Effluent Treatment Facility (LETF) is an industrial wastewater treatment facility at the Savannah River Site (SRS). It is designed to treat liquid effluents from nickel plating and aluminum forming operations in the Reactor Materials Department (RMD). The mission of the RMD was to manufacture depleted uranium targets (slugs) for plutonium production, lithium/aluminum targets for tritium production, and enriched uranium assemblies as the neutron sources for the SRS reactors. One of the primary streams treated in the LETF is dilute rinses from nickel plating operations of the depleted uranium targets. The LETF utilizes controlled precipitation and enhanced filtration to remove the contaminants (primarily aluminum, nickel, and depleted uranium) from the liquid effluents. The precipitated materials are filtered and intrained by a narrow range particle size filtration aid, expanded perlite. Since the resulting filtercake contains "a wastewater treatment sludge from electroplating operations", it is considered a "listed" F006 hazardous waste. As the filtercake contains depleted uranium (100 - 10,000 mg/kg) it is considered a radioactive waste. The filtercake is transferred to Resource Conservation and Recovery Act (RCRA) interim status treatment and storage tanks, the M-Area Process Waste Interim Treatment/Storage Facility (PWIT/SF). The filtercake is pumped to the storage tanks via a continuously recirculating transfer line, to maintain the filtercake solids in suspension.

The Westinghouse Savannah River Company (WSRC) Environmental Protection Department (EPD) determined that some materials or equipment removed from service during maintenance activities would be considered "debris", as defined by the August 1992 Environmental Protection Agency (EPA) debris rule (1). It should be noted that only materials intended to be discarded, and could not be reused, would meet the definition of debris. Since the M-Area transfer line and pumps had contacted the F006 wastes, the resulting debris would "contain" a listed waste, and must be treated to meet all of the Land Disposal Restrictions and RCRA Subtitle C regulations prior to disposal. Since there is no current facility able to treat such a listed/mixed waste, the debris would have to have been stored for years, until a treatment facility is designed and constructed at the SRS.

The EPA had previously issued a Case-by-Case Capacity Variance for a generic, one-time extension of the LDR effective date (from May 8, 1992 to May 8, 1993) applicable to all persons managing hazardous debris (2). In order for a generator to utilize this extension, certain information must be included in the facility's operating record at the time the hazardous debris is generated. This information includes:

- Name, mailing address, location, and EPA identification No. of the facility,
- Description of the waste,
- Waste generation rates and estimated inventories,
- A written plan on how the facility will obtain adequate treatment capacity,
- A schedule of the plans to design, construct, and obtain the necessary permits for the treatment facility,
- Certification that a landfill, if used, meets the Requirements of 40 CFR 268.5(h)(2).

The planned facility, the Hazardous Waste/Mixed Waste Disposal Facility (HW/MWDF) is not anticipated to be operational prior to the year 2002. In addition, the only applicable treatment techniques for the mixed F006 type of debris would be Chemical Extraction or Immobilization. Immobilization is not attractive, as the final treated material must still be disposed as a hazardous waste, and treatment and disposal costs for such mixed wastes is extremely expensive. Chemical Extraction would render the debris non-hazardous, but the amount of such debris anticipated to be generated is quite small (tens of cubic meters), so that inclusion of an such operation in the HW/MWDF for the F006 listed wastes would not be cost effective. In fact, this type of chemical extraction treatment equipment is not in the current scope of the HW/MWDF, so a scope change would be required if such mixed debris were to be chemically treated at the SRS.

It was decided that utilizing the generic Case-by-Case extension allowed by the EPA was not feasible for the anticipated debris. Certification of the landfill to meet the minimum requirements was not cost effective for the small volume of waste. Modifying the Scope of Work and design of the HW/MWDF to allow continued storage, was also unattractive. Therefore, a technique to treat the mixed waste debris as generated was developed, which allowed disposal of the treated materials to the SRS Low Level Radioactive Solid Waste Disposal Facility (SWDF).

REGULATORY BACKGROUND

Debris Rule

In the EPA final rule promulgated August 18, 1992, "debris" is defined as:

> "solid material exceeding a 60 mm (~2.5 in) particle size that is intended for disposal and that is: A manufactured object; or plant or animal matter; or natural geologic material."

Process residuals such as melted slag and wastewater treatment sludges are NOT debris. However, "a

mixture of debris that has not been treated to the standards provided by 40 CFR 268.45 (3) and other material is subject to regulation as debris if the mixture is composed primarily of debris, by volume, based on visual inspection".

Hazardous debris is defined as :

> "debris that contains a hazardous waste listed in subpart D of part 261 of this chapter, or that exhibits a characteristic of hazardous waste identified in subpart C of part 261 of this chapter".

The EPA specifically addressed the "contained in" determination in the preamble to the final rule. They stated that "In adopting the definition that debris containing listed hazardous waste is regulated under Subtitle C, EPA is codifying the 'contained in' principle".

Contaminated pumps and pipes. Based on the proposed debris rule published 1/9/92, the EPA received a number of requests (SRS's among them) to clarify what discarded industrial equipment would be included in the definition of debris. The EPA stated in the preamble to the final rule (3) that:

> "a discarded pump or filter used to treat a waste is debris, but the waste pumped or filtered is not debris. Although some filtered or pumped waste will contaminate the pump or filter, (indeed, that is the basis for subjecting the filter or pump to the treatment standards), the contaminated pump or filter will virtually always be composed primarily of debris rather than waste and would so be classified as debris".

The EPA reiterated this point in the discussion of treatment technologies (3), in which they stated that:

> "Note that the performance or design and operating standards must be met for all debris surfaces that are contaminated with hazardous waste. Thus, if a pipe or pump was used to manage hazardous waste, the performance standards must be met for the inside surfaces of the pipe or pump" (emphasis added).

Extraction technologies and "clean debris surface". The chemical extraction technologies identified by the EPA are:

> water washing and spraying; liquid phase solvent extraction; and vapor phase solvent extraction. The performance standards for these technologies are based on the dissolution of the contaminants into the cleaning solution. Water sprays or water baths will effectively treat debris when sufficient temperature, pressure, residence time, agitation, surfactants, acids, bases, and/or detergents are used to meet the performance standards.

The rule requires that the debris must be treated to a "clean debris surface". A "clean debris surface" is defined as:

> "the surface, when viewed without magnification, shall be free of all visible contaminated soil and hazardous waste except that residual staining from soil and waste consisting of light shadows, slight streaks, or minor discolorations, and soil and waste in cracks, crevices, and pits may be present provided that such staining and waste and soil in cracks, crevices, and pits shall be limited to no more than 5% of each square inch of surface area".

The debris rule points out that any residues resulting from the treatment of debris must be managed appropriately, i.e.: either treated as hazardous wastes and/or treated in a RCRA treatment facility or a wastewater treatment facility permitted under the Clean Water Act.

Treatment In Containers

In March, 1986, the EPA issued a final rule on management of hazardous wastes (5). The rule included regulations pertaining to small quantity generators and the on-site treatment of hazardous waste by small quantity generators. In the preamble, the EPA stated that:

> "Of course, no permitting would be required if a generator chose to treat their hazardous waste in the generator's accumulation tanks or containers in conformance with the requirements of Part 262.34 and Subparts J or I of Part 265" (of the hazardous waste regulations for interim status facilities). "Nothing in Part 262.34 precludes a generator from treating a waste when it is an accumulation tank or container covered by that provision".

The requirements for a generator accumulating up to 55 gallons of hazardous waste are:

- the accumulation containers must be "at or near" the point of generation [40 CFR 262.34(c)(1)],
- the containers must be under the control of the operator generating the waste [40 CFR 262.34(c)(1)],
- the containers must be in good condition per 265.171 [40 CRF 262.34(c)(1)(i)]
- the container or its liner must be compatible with the waste per 265.172 [40 CFR 262.34(c)(1)(i)],
- the container must always be closed during storage, except when necessary to add or remove waste per 265.173(a) [40 CFR 262.34(c)(1)(i)],
- the generator must mark the container with the words "Hazardous Waste" or with other words that identify the contents of the containers [40 CFR 262.34(c)(1)(ii)].

The South Carolina Department of Health and Environmental Control (SCDHEC) has provided guidance to WSRC that more than one accumulation container may be present in such "satellite" accumulation areas, as long as the same type of waste is being accumulated, and the total volume does not exceed 55 gallons of hazardous waste. However, SCDHEC has also stated that the waste must be maintained in its original accumulation container, i.e.; it can not be consolidated from small containers to a larger container in a satellite area. This type of consolidation is only allowed in an 90 day accumulation area, where hazardous wastes are being accumulated and consolidated to facilitate shipment to a treatment or disposal facility.

The requirements of 262.34 are more extensive with respect to a generator accumulating more than 55 gallons of hazardous waste in a 90 day accumulation area. The requirements for treatment in containers in 90 day accumulation areas include:

- the generator must comply with 265 Subpart I for container storage [40 CFR 262.34(a)(1)(i)],
- the date when accumulation begins is clearly marked on each container [40 CFR 262.34(a)(2)],
- each container is clearly labeled or marked "Hazardous Waste" [40 CFR 262.34(a)(3)],
- the generator must comply with the Preparedness and Prevention requirements of 265 Subpart C [40 CFR 262.34(a)(4)],
- the generator must comply with the Contingency Plans and Emergency Procedures requirements of 265 Subpart D [40 CFR 262.34(a)(4)],
- the generator must comply with 265.16 with respect to training of the personnel managing the hazardous waste [40 CFR 262.34(a)(4)], and
- the generator must develop and follow a written waste analysis plan per 268.7(a)(4) which describes the procedures that the generator will carry out to comply with the treatment standards, if the generator is treating waste to meet applicable treatment standards* [40 CFR 262.34(a)(4)]:

- the plan must be kept onsite in the generator's records,
- it must be based on a detailed chemical/physical analyses of the wastes being treated,
- provide all information necessary to treat the wastes, and
- the plan must be filed with the regulator 30 days prior to starting treatment.

* Note that "Generators treating hazardous debris under the alternative treatment standards of Table 1, Part 268.45, however, are not subject to these waste analysis plan requirements".

The applicable requirements of the 268.7 regulations are:

- if the generator is treating debris using the extraction or destruction technology provided by Table 1, Part 268.45, the generator is subject to the notification and certification requirements of part 268.7(d):

-(d)(1) A one time notification must be submitted to the Director or authorized state with the following information:
- (d)(1)(i) name and address of subtitle D facility receiving the treated debris,
- (d)(1)(ii) description of debris as generated, including the applicable EPA Hazardous Waste No.,
- (d)(1)(iii) the technology used to treat the debris.

-(d)(3) The following documentation and certification requirements must be met:
- (d)(3)(i) records must be kept of all inspections and analyses of the treated debris,
- (d)(3)(ii) records must be kept of the key operating parameters of the treatment unit, and
- (d)(3)(iii) the following certification must be maintained in the facility's files: "I certify under penalty of law that the debris has been treated in accordance with the requirements of 40 CFR 268.45. I am aware that there are significant penalties for making a false certification, including the possibility of fine and imprisonment".

Since the on-site SRS low level radioactive Solid Waste Disposal Facility (SWDF) is not permitted as a Subtitle D facility, it was not clear whether the notification to EPA described under 268.7(d)(1) was required of the SRS. The written job-plan for the in-container treatment specified the final disposal location.

TREATMENT OF F006 DEBRIS IN CONTAINERS AT THE SRS

Based on these regulations and guidance, WSRC determined that two pumps and several sections of associated carbon steel pipe in the M-Area LETF would be considered debris when removed from service. The WSRC Environmental Protection Department contacted the Environmental Protection Agency (EPA), Region IV with respect to whether the piping and pumps could be flushed in place prior to removal. The EPA agreed that since the piping is part of a wastewater treatment facility, WSRC could flush the piping while still in-situ, using a water wash which would meet the debris rule treatment technology. This could be accomplished under the coverage provided by the wastewater treatment permit, and would not require a RCRA permit for the activity. Once the in-situ water washing technology was performed, the debris subsequently dismantled from the wastewater treatment system could meet the treatment standard for debris "as generated" and would not require further treatment as long as it met the performance standard to "clean debris surface" as defined in the debris rule. WSRC would maintain documentation of how the water washing technology meets the debris rule standard. The residuals from the in-situ washing would be routed to the RCRA storage tanks to be subsequently treated and stabilized to meet the F006 land disposal

restriction treatment standards.

It was also determined with the EPA that RCRA regulations would allow for further treatment in accumulation containers if the initial in-situ water washing step did not result in a "clean debris surface". This subsequent step would not require a RCRA permit since it would be done in the accumulation tank or container.

Description Of Equipment Removal and Cleaning

After all the regulatory "hoops" had been defined, and the proposed plan had been discussed with the EPA, the actual work was anti-climatic. A written project plan was prepared, which addressed the regulatory and documentation requirements.

Each pump and its associated piping was flushed in-place with 1500 gallons of rinse water. The rinse water was transferred to the IT/SF. The piping was then removed, and cut into 2 ft sections to allow inspection of the inside surface. The cut pipe pieces were immediately placed in a 55 gallon drum, labeled with the identification of the material. The fines from the sawing were flushed to the nearby sump, then to the slurry hold tank, and subsequently to the interim status RCRA IT/SF storage tanks.

The cut pipe pieces were inspected to determine if they met the "clean debris surface" definition as generated. Unfortunately, some accumulation could still be detected. The inside surface of each cut pipe was then scrubbed with a wire brush, rinsed, and re-scrubbed and rinsed, and then inspected by the WSRC "systems engineer" for the DETF, and confirmed to meet the "clean debris surface" definition. A similar procedure was conducted for the two pumps, except that the pumps were dismantled so that all interior surfaces could be scrubbed and rinsed (inside the 55 gallon drum). The rinses from the 55 gallon drum were emptied to the sump and transferred to the interim status IT/SF tanks. Since the treated debris had originated in a "Radioactive Control Area" (RCA), the debris was considered potentially radioactive, and was discarded to the low level radioactive Solid Waste Disposal Facility (SWDF). The 55 gallon drum was rinsed, emptied, and discarded to the low level radioactive Solid Waste Disposal Facility (SWDF) (as an empty container). The drums rinses were transferred to the interim status IT/SF tanks.

The documentation was maintained on file at the SRS.

SUMMARY

The SRS successfully demonstrated that equipment contaminated with listed F006 mixed hazardous waste could be cleaned and discarded as low level radioactive waste, without obtaining a RCRA treatment permit. The estimated cost saving for this exercise was approximately $4500, based on the current estimate of $625/ft^3 for storage, treatment, and disposal of mixed wastes at the SRS (vs. $20/ft^3. for disposal of Low Level radioactive waste). More importantly, a precedent was established for treatment and disposal of larger volumes of similar mixed F006 waste debris from the M-Area wastewater treatment facility which could be generated in the future. This as-generated treatment technique will eliminate the long term storage of this mixed waste debris, and will eliminate the need for this type of treatment capacity in the future Hazardous Waste/Mixed Waste Treatment Facility.

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RADIOLOGICAL IMPACTS OF LANDFILL DISPOSAL OF ACTIVATED CONCRETE DEBRIS FROM THE STANFORD LINEAR ACCELERATOR CENTER

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ABSTRACT. The U.S. Department of Energy (DOE) is confronting a major policy decision regarding the disposal and treatment of radioactive and mixed wastes. The DOE's San Francisco Operations Office (DOE/SF) has proceeded with a systematic approach to classify specific radioactive materials as *below regulatory concern* (BRC) and to dispose of these wastes as nonradioactive materials at municipal landfills. Although the issues surrounding the classification of radioactive materials as BRC are controversial, the State of California has concurred with the DOE/SF's case-by-case approach to disposing of detectable amounts of radioactive waste in municipal landfills. This paper discusses our methodology for obtaining regulatory approval for the disposal of suitable radioactive waste in a municipal landfill.

INTRODUCTION

The U.S. Department of Energy's San Francisco Operations Office (DOE/SF) has evaluated the potential radiological impacts of municipal landfill disposal of low-level radioactive debris generated by structural modifications at the Stanford Linear Accelerator Center (SLAC) in Menlo Park, California. The DOE/SF submitted samples of the debris, which consisted of concrete and rebar (structural reinforced steel bars and materials), to two DOE laboratories for radiological analysis. The radionuclide data from these analyses provided input to the IMPACTS-below regulatory concern (BRC) computer code, which was used to determine the radiological doses to individuals (workers) and the general population that could be expected as a result of disposing of the debris as nonradioactive waste at the Browning Ferris, Inc. Ox Mountain municipal landfill in nearby Half Moon Bay. The radiological impacts were then assessed, through all pathways of exposure, with regard to a lifetime risk of fatal cancers that could be expected. For the maximum exposed individual (worker), the risk from the disposal of the SLAC debris was approximately 2,000 times less than the risk from natural radiation. For an individual in the general population, the risk was approximately 1.8 billion times less than the risk from natural radiation.

Because the risk posed by commercially disposing of the SLAC debris as nonradioactive waste (i.e., BRC) was shown to be extremely low, the State of California (a Nuclear Regulatory Commission or NRC Agreement State) has issued an exemption allowing the debris to be disposed in the Ox Mountain landfill, without regard to its radioactivity. Previously, the SLAC debris had been evaluated for Resource conservation and Recovery Act (RCRA)- and California-listed hazardous constituents. As a result of that evaluation, the U.S. Environmental Protection Agency or EPA (Region 9) and the California Department of Health Services concurred with the DOE/SF that the debris was not a mixed waste. However, because a SLAC employee had protested a similar disposal at the Ox Mountain landfill site, claiming that the debris was actually a mixed waste, the Environmental Protection Agency and the State of California investigated the proposed disposal. They concluded that the DOE/SF, and all state and federal agencies, had complied with and fulfilled the regulatory requirements for disposing of the debris as nonradioactive, nonhazardous

waste at a municipal landfill. This report documents the risks associated with the disposal of this waste at a municipal landfill and the DOE/SF's compliance with all requirements of federal and state regulations and DOE policy. Note that the DOE has issued a moratorium on the disposal of hazardous wastes that have any radioactivity added. The Performance Objective of this moratorium does not apply to this concrete/rebar waste stream because (1) it is not an RCRA, California hazardous, or Toxic Subtand Control Act (TSCA) waste; and (2) the Performance Objective states that ". . . any resulting waste *is not* a radioactive waste if it meets the following conditions: . . . wastes specifically exempted by the EPA, DOE, or NRC regulations. . . ." In addition, DOE Order 5820.2A, Section i(6) states that "waste containing amounts of radionuclides below regulatory concern, as defined by federal regulations, may be disposed without regard to radioactivity content."

WASTE CHARACTERIZATION OF SLAC DEBRIS

SLAC is located on 1.72 km^2 (426 acres) of Stanford University land in an unincorporated area of San Mateo County. Modifications to SLAC's 3.22-km-long (2 mi) Linear Accelerator (LINAC) generated about 10 m^3 (~350 ft^3) of activated concrete/rebar debris. LINAC's concrete nose structure, located in the beam switchyard, was demolished and pulverized to make space for the installation of 19 m of muon shielding (iron) for the final Focus Test Beam project. The trapezoidal-shaped nose structure was about 8.5 m long (28 ft) and 3 m high (10 ft). The upstream end was about 20 m wide (65 ft), and the downstream end was about 5 m wide (16 ft). During the operation of LINAC, the concrete/rebar in the nose structure became activated by high energy electrons and protons. The DOE/SF asked both SLAC and the Lawrence Livermore National Laboratory (LLNL) to perform independent radiological analyses on samples of the activated concrete/rebar debris.

SLAC Analysis

SLAC analyzed samples of the pulverized and homogeneously mixed concrete/rebar debris using a 5- × 5-cm-high (2- × 2-in.) purity germanium detector with a 13% relative efficiency and an approximate 2 keV full width at half-maximum (FWHM) when measured at 1.33 MeV. All detector efficiency calibrations were performed with traceable sources from the National Institute of Standards Testing (NIST). Spectrums were accumulated with Canberra S-100 software and then analyzed with microSAMPO advanced gamma-spectrum analysis software. SLAC identified cobalt (^{57}Co, ^{60}Co), scandium (^{46}Sc), manganese (^{54}Mn), and sodium (^{22}Na) as the principal radioisotopes in the concrete shield with half-lives greater than a few days. Potassium (^{40}K), a naturally occurring radionuclide, was also identified. Table 1 lists the isotopes identified by SLAC and their overall average concentration of radioactivity.

LLNL Analysis

After the SLAC analysis, nine samples of the debris were separated into concrete, sand/gravel, and wire/rebar and submitted to LLNL for analysis. In addition, three samples of background (unexposed) concrete/rebar were submitted for comparison to the activated concrete/rebar. Using a separate, independent laboratory for the second analysis allowed us to verify the accuracy of the SLAC analysis results. In addition to the radioisotopes identified by SLAC, LLNL identified zinc (^{65}Zn), cesium (^{134}Cs), and europium (^{152}Eu, ^{154}Eu). Table 2 lists the isotopes identified by LLNL and their overall average concentration of radioactivity.

WASTE DISPOSAL ANALYSIS USING THE IMPACTS-BRC CODE

The *Low-Level Radioactive Waste Policy Amendments Act* of 1985 mandated that the NRC establish policies and procedures for acting on petitions to classify very low-level radioactive waste streams as BRC. To fulfill

Table 1. Results of the SLAC radiological analysis of debris samples (corrected to September 14, 1992). Concentrations of radioactivity are in pCi/g ± SD (pico-curies/gram ± standard deviation).

Isotope	Original Decay	Recount 09/14/92	Overall average concentration
^{22}Na	1.002 ± 0.139	8.950 ± 4.738 × 10^{-01}	9.49 ± 0.76 × 10^{-01}
^{46}Sc	5.948 ± 4.613 × 10^{-03}	NA	5.95 ± 4.61 × 10^{-03}
^{54}Mn	3.440 ± 1.266 × 10^{-01}	7.370 ± 5.841 × 10^{-01}	5.41 ± 2.78 × 10^{-01}
^{57}Co	6.795 ± 1.195 × 10^{-02}	6.780 × 10^{-01}	3.73 ± 4.31 × 10^{-01}
^{60}Co	2.398 ± 1.447	2.420 × 1.616	2.41 ± 0.02
^{40}K	NA	3.175 × 2.356	3.18 ± 2.36
		Total radioactivity[a]:	7.46 pCi/g

[a]Not including ^{40}K.

Table 2. Results of the LLNL radiological analysis of debris samples. Concentrations of radioactivity are in pCi/g ± SD.

Isotope	Concrete	Sand/gravel	Wire/rebar	Background concrete
^{22}Na	9.040 ± 0.477 × 10^{-01}	2.800 × 10^{-01}	0.000	0.000
^{46}Sc	2.000 ± 0.008 × 10^{-02}	0.000	0.000	0.000
^{54}Mn	1.346 ± 1.296	9.000 × 10^{-02}	3.067 ± 3.490	0.000
^{57}Co	4.333 ± 0.029 × 10^{-02}	1.000 × 10^{-02}	1.280	0.000
^{60}Co	2.626 ± 1.759	2.000 × 10^{-02}	5.467 ± 8.277	0.000
^{65}Zn	7.667 ± 0.031 × 10^{-02}	0.000	0.000	0.000
^{134}Cs	5.000 ± 0.033 × 10^{-02}	1.000 × 10^{-02}	0.000	0.000
^{152}Eu	1.290 ± 0.832	1.300 × 10^{-01}	0.000	0.000
^{154}Eu	1.475 ± 0.068 × 10^{-01}	0.000	0.000	0.000
^{40}K	8.422 ± 1.430	9.070	0.000	7.495 ± 0.276
Total radioactivity[a]:	6.504	5.400 × 10^{-01}	9.814	0.000

[a]Not including ^{40}K.

this mandate, the NRC developed policy statements and staff implementation plans that would allow the use of the IMPACTS-BRC computer code (1,2) to independently evaluate petitions requesting that particular low-level radioactive waste streams be exempted from NRC (and Agreement States) regulations. The NRC contracted Sandia National Laboratories, Albuquerque, to provide technical support to evaluate, validate, and document a defensible version of this code. IMPACTS-BRC Version 2.0, which is written in Fortran and runs on a PC using MS-DOS, is often used to evaluate these petitions.

The IMPACTS-BRC code can calculate the radiological doses to individuals and to the population through all exposure pathways (e.g., direct exposure to gamma radiation, and the ingestion and inhalation of radionuclides) for a specific waste processing option (e.g., on-site and off-site incineration, sanitary landfill disposal, and hazardous waste landfill disposal). The radiological dose results for individuals and the population are given in the whole body effective dose equivalent, which is hereafter referred to as *dose* and is measured in mrem/yr or person-mrem/yr (Table 3).

Table 3. Description of ICRP-30 effective dose equivalents calculated by the IMPACTS-BRC code.

Calculated dose	Units[a]	Data output abbreviations
Transportation		
Maximum transportation worker dose	m	TR-MAX
Total dose to transportation workers	p-m	TR-OCC
Total population dose from transportation	p-m	TR-POP
Intruder		
Intruder dose from construction activities at closed site	m	INT-CO
Intruder dose from agricultural activities at closed site	m	INT-AG
Exposed waste		
Intruder initiated airborne dose to the total population	p-m	IN-AIR
Erosion initiated airborne dose to the total population	p-m	ER-AIR
Maximum intruder initiated waterborne dose to an off-site individual	m	IN-WAT
Maximum erosion initiated waterborne dose to an off-site individual	m	ER-WAT
Incineration and disposal operations		
Total population dose from incinerator operation	p-m	IC-POP
Maximum off-site individual dose from incinerator operation	m	IC-IND
Total worker dose from incinerator operation	p-m	IC-WOR
Maximum worker dose from incinerator operation	m	IC-MWR
Total population dose from disposal operation	p-m	OP-POP
Maximum off-site individual dose from disposal operation	m	OP-IND
Total worker dose from disposal operation	p-m	OP-WOR
Maximum worker dose from disposal operation	m	OP-MWR
Leachate accumulation		
Maximum off-site individual dose from leachate discharge	m	LA-OPS
Maximum off-site individual dose from leachate flow	m	LA-OVF
Total population airborne dose from evaporator operation	p-m	LA-AIR
Groundwater		
Intruder dose from contaminated well water	m	INT-WELL
Maximum off-site individual dose from contaminated well water	m	POP-WELL
Maximum off-site individual dose from contaminated surface water	m	POP-SURF

[a] m = mrem/yr; p-m = person-mrem/yr.

Using the IMPACTS-BRC computer code, the DOE/SF estimated the radiological doses to individuals and to the population resulting from the disposal of the SLAC concrete/rebar debris at the Ox Mountain landfill. The IMPACTS-BRC code uses three ASCII data input files in fixed-field format and a reference radionuclide inventory to calculate estimated doses. The first input file, TAPE1.DAT, contains nuclide-specific data. Generally, this file does not require user editing, and it was not changed for the SLAC dose calculations. The second input file, TAPE2.DAT, contains data for the reference environments and facilities and may require user editing. For these calculations, some of the values in the file were modified. The third input file, TAPE5.DAT, contains data for the waste type and chosen treatment and disposal options. The user of the code must create this file by choosing from among the treatment and disposal options available in the code and by inputting the values appropriate to the waste type. Finally, for these calculations the data for the code's reference radionuclide inventory were derived from the SLAC and LLNL radionuclide analyses of the activated concrete/rebar debris.

Nuclide-Specific Data

The TAPE1.DAT file contains nuclide-specific data, such as the retardation coefficients and the dose conversion factors (DCFs), for each of 85 radionuclides. This data is used to calculate the radiological impacts resulting from ingestion, inhalation, and external volume, area, and air-immersion pathways. The DCFs from the volume pathway were calculated using the computer program MICROSHIELD. All other DCFs were obtained from ICRP-30 (Parts I-IV).

Reference Environments and Facilities

The TAPE2.DAT file contains data for the code's reference environments and facilities. To ensure conservatism in the dose calculations, most of the code's default values were used for these calculations. However, some values were changed to represent more accurately the environmental conditions of San Mateo County, where the waste would be disposed.

The default value for the population density is 610 persons/mi^2. Note that the data input units are expressed in English nomenclature because the code cannot accept SI units. The population distribution in 10 mi concentric zones from SLAC to the Ox Mountain landfill is 200,000 persons within 236 mi^2 (3). Thus, the average population density is about 850 persons/mi^2. However, because the majority of the route from SLAC to the Ox Mountain landfill site is in an area with a below-average population density, the default value of 610 persons/mi^2 was used to calculate the population dose from transportation.

The default value for the distance between the waste generator's site and the waste disposal site is 100 mi. For these calculations, a distance of 30 mi was chosen as being representative of the distance between SLAC and the Ox Mountain landfill.

The default value for the volume of BRC waste disposed of annually is 2.96×10^4 m^3/yr. The doses calculated by the code are based on the effective radionuclide concentration in the waste. The effective radionuclide concentration is the quotient of the radioactivity (measured in curies) disposed of annually divided by the volume of the nonradioactive constituents. Oztungli and Roles (4) give a value of about 0.7 metric tons/person/yr as being typical of refuse disposal at sanitary landfills. If the Ox Mountain landfill site also receives the refuse generated by one-third of the residents of San Mateo County, and if the average density of this waste is 0.59 g/cm^3, (4) then the annual disposal capacity would be 2.37×10^5 m^3/yr, which is almost an order of magnitude greater than the default value. To ensure conservatism in the dose calculations, the default value was used.

The code's default landfill is on 25 acres and operates 280 days a year for 20 years. The code assumes that there is one foreman, three equipment operators, four laborers, and two gate/traffic controllers. The personnel default data are on the order of a single full-time worker. This means that the single worker has

a number of jobs at the landfill and thus spends a fraction of his time at each job. Based on this site data, the impacts to each worker are calculated, and the total impacts are summed and divided by the total number of workers (i.e., ten workers). Because there is only one worker, the maximum worker impact and the total worker impact are equal. The IMPACTS-BRC code is set up to evaluate a continual disposal operation. Because the SLAC concrete/rebar disposal is a one-time operation, the landfill parameters were modified so that the operational life of the facility is 1 yr, after which time the facility would be closed (i.e., no additional radioactive concrete/rebar would be introduced) and administratively controlled for 19 yr. These parameters more closely approximate the case of sending a one-time waste stream (non-reoccurring), which would then be administratively controlled for the remainder of the landfill lifetime (19 yr).

Waste Type and Treatment and Disposal Options

The TAPE5.DAT file contains data for the treatment and disposal options and the physical, chemical, and radiological characteristics of the waste stream(s). In addition to specifying the facility location and treatment and disposal option, the user must specify the mass, volume, and density of the waste being disposed, the radionuclide concentrations, the waste dispersibility, and the fraction of combustible waste. The TAPE5.DAT parameter values chosen for the SLAC dose calculations are shown in Table 4.

Table 4. TAPE5.DAT parameter values chosen for the SLAC dose calculations. These values are used to determine the doses for each waste stream pathway.

Data input	Printout name	Parameter name	Value	Comments
[TDIS(IQ)]	—	Transportation distance to facility	30	In miles
[TVEL(IQ)]	—	Transportation velocity to facility	45	In miles per hour
[ILFE]	LIFE	Operational life of facility	01	In years
[IR]	REGN	Regional index	02	Southeast: humid, moderate soil permeability, moderate population density
[IPOP]	IPOP	Facility environmental index	02	Urban site
[IOFL]	OVFL	Overflow index	01	Calculate overflow impacts
[IDAT]	DATA	Disposal/treatment population	02	Environmental parameters that represent a very conservative (poor performance) site for waste disposal.
[IINS]	INST	Institutional control period	19	In years
[NSTRD]	NSTR	Number of waste streams	01	Rebar and concrete are separate

Table 4. (Continued.)

Data input	Printout name	Parameter name	Value	Comments
[BAS(1,1)]	—	Mass of waste stream	21.7	Weight of concrete (in metric tons)
[BAS(1,2)]	DENSITY	Density of waste stream	2.4/7.85	Grams/cm^3; metric tons/m^3 (Both concrete/rebar)
[BAS(1,3)]	—	Volume of waste stream	9.04	In cubic meters
[ID]	—	Dispersability index	02	Moderate dispersability
[IA]	—	Accessibility index	01/02	Ordinary waste; activated metals
[IK1]	—	Packaging index	0	Not packaged (bulk)
[IK2]	—	Packaging recycling index	0	Not packaged (bulk)
[IP][a]	PROCESS	Processing index	01	Disposal; no sorting option
—	IXS	Distribution index	—	—
[IX1]	—	Number of shipping vehicles	01	Maximum route exposure to handler
[IX2]	—	Percent of load radioactive	100	—
[IX3]	—	Number of incinerators	0	—
[IX4]	—	Number of disposal facilities	01	BFI's Ox Mountain landfill, Half Moon Bay, CA
—	ICS[a]	Composition index	—	—
[IC1]	—	Percent of load combustible	0	Both concrete and rebar
[IC2]	—	Percent of load glass	0	Both concrete and rebar
[IC3]	—	Percent of metal waste	0/100	Concrete; rebar
[IC4]	—	Percent of load that is other waste	0	Activated concrete

[a]The composition indices are used only for sorting and recycling. Valid if IP > 2.

The facility and environmental parameters for TAPE5.DAT data were chosen to ensure conservatism in the dose calculations. For example, a humid location with permeable soil was selected for the landfill's region index (Ox Mountain is located near the San Francisco Bay), which resulted in relatively large estimated doses for groundwater pathways; an urban environment, rather than a rural environment, was selected for the landfill location, which resulted in larger population doses; and one truck was assumed to haul the 10 m^3 (~350 ft^3) of activated concrete at an average speed of 45 mph to the disposal site, which maximized the estimated dose to the transportation worker.

Reference Radionuclide Inventory

The IMPACTS-BRC code used two radionuclide inventories for the SLAC waste disposal analysis. A calculation was first performed using an inventory derived from the average specific activities for the principal radionuclides in the homogeneous rubble pile analyzed by SLAC. A second calculation was performed using an inventory derived from the average specific activities for the principal radionuclides in the various samples analyzed by LLNL; it was assumed that the samples of concrete rubble, sand/gravel, and wire/rebar in different locations would be uniformly mixed when hauled and disposed of at the landfill. The average specific activities are the sums of the individual activities of the nuclides present in measurable amounts over background levels.

RESULTS

The IMPACTS-BRC code was run twice. The first calculation used the radionuclide inventory derived from the SLAC analysis, and the second calculation used the radionuclide inventory derived from the LLNL analysis. The radionuclide contribution from ^{40}K was not included in either calculation because ^{40}K is from natural sources not introduced by DOE operations. The following sections summarize and compare the estimated dose results from the two calculations. Note that the estimated doses for the handling and treatment disposal operations were assumed to be proportional to the radionuclide concentration of the waste; this concentration was determined by dividing the radionuclide inventory in the activated debris by the total volume of waste (ordinary and radioactive) in the Ox Mountain landfill.

Summary of Estimated Doses Using SLAC and LLNL Radionuclide Data

The results from the calculation using the SLAC radionuclide data showed that the two largest individual doses would be received by the truck driver who transports the waste and the maximum exposed worker at the landfill site. The estimated dose to the truck driver is 3.29×10^{-02} mrem/yr, and the estimated dose to the maximum exposed landfill worker is 4.11×10^{-03} mrem/yr. The estimated doses to people who intrude on the disposal site after site closure and who engage in construction or agriculture on the disposal site after site closure are 7.08×10^{-05} and 3.36×10^{-04} mrem/yr, respectively. Individual doses to other members of the public from direct exposure, or from air or water pathways, are extremely low (3.04×10^{-08} mrem/yr for the individual and 1.76×10^{-06} person-mrem/yr for the population) and are considered negligible when compared to natural background radiation. Table A-1 lists all the estimated maximum annual individual doses for this calculation (Appendix A).

The results from the calculation using the LLNL radionuclide data showed that the estimated dose to the truck driver is 5.97×10^{-02} mrem/yr, and the estimated dose to the maximum exposed landfill worker is 7.41×10^{-03} mrem/yr. The estimated doses to people who intrude on the disposal site after site closure and who engage in construction or agriculture on the disposal site after site closure are 3.60×10^{-04} and 1.70×10^{-03} mrem/yr, respectively. Individual doses to other members of the public from direct exposure, or from air or water pathways, are considered negligible (6.5×10^{-08} mrem/yr for the individual and 3.76×10^{-06} person-mrem/yr for the population). Table A-2 lists all the estimated maximum annual individual doses for this calculation (Appendix A).

Although the estimated doses based on the LLNL radionuclide data are small, they are somewhat higher than the estimated doses based on the SLAC radionuclide data. The higher doses are due to the ~30% higher concentration of isotopes in the LLNL radionuclide data. However, the difference is small between the two analyses, and within the statistical error margin of equipment.

Data Comparison

Table 5 shows a comparison of the summed dose results from the two calculations using the IMPACTS-BRC code. The most conservative (worst-case) doses indicate that the largest estimated doses would be received by the workers at the landfill facility, the transportation workers, and population residing along the route leading from SLAC to the Ox Mountain disposal site. The cumulative population dose from landfill disposal of all the activated concrete is estimated to be less than 5.0×10^{-06} person-mrem/yr (0.005 person-mrem/yr), which is approximately nine orders of magnitude less than the annual dose to that same

Table 5. IMPACTS-BRC comparison (concrete and rebar).

	Effective dose equivalent	
Affected population	SLAC data	LLNL data
Transportation/handler	3.3×10^{-02} mrem/yr	6.0×10^{-02} mrem/yr
Transportation/population	4.3×10^{-02} person-mrem/yr	7.8×10^{-02} person-mrem/yr
Disposal site/worker	4.1×10^{-03} mrem/yr	7.4×10^{-03} mrem/yr
Disposal site/intruder	4.1×10^{-04} mrem/yr	2.1×10^{-03} mrem/yr
Off site/individual	3.0×10^{-08} mrem/yr	6.5×10^{-08} mrem/yr
Off site/population	1.8×10^{-06} person-mrem/yr	3.8×10^{-06} person-mrem/yr

population from natural background radiation levels (i.e., one one-billionth of natural background radiation).

Note that for the data comparison, the radioactivity detected by SLAC in the concrete rubble was assumed to also be present in the rebar at the same specific activity. SLAC had analyzed representative samples of the concrete rubble without differentiation of the debris, whereas LLNL had analyzed samples that were differentiated between concrete, background concrete, and rebar debris.

RISK ASSESSMENT

After the radiological doses were estimated using the IMPACTS-BRC code, the risk posed by disposing of the SLAC waste at the Ox Mountain landfill was analyzed. For almost 40 years, regulatory agencies have used risk assessment as a decision-making tool to determine whether or not an operation is "acceptable" based on the associated risk. If the calculated risk to the public and the environment is too high, the operation may be considered "unacceptable." If the calculated risk is below the statutory limit, the risk is usually judged insignificant, and the operation or practice is allowed.

Using any risk model to calculate radiological risk estimates for low doses and dose rates involves making certain assumptions that must be validated. Because the generally preferred risk models are a linear function of dose, little uncertainty should be introduced on this account, but departure from linearity cannot be excluded at doses below the range of observation. The NRC acknowledges that these uncertainties in risk

estimates are large at low doses, and the coefficient adopted in Table 6 is based on the BIER V committee's conservative risk coefficient of 5×10^{-4}/rem causing excess fatal lifetime cancers for low linear energy transfer (LET) radiation. The NRC has concluded that in view of the uncertainties involved in risk assessment at low doses, the average dose to individuals in a critical group affecting a limited population should be less than 10 mrem/yr (0.1 mSv/yr). The NRC also concluded that the average dose to individuals in a critical group affecting a large number of the population (e.g., the widespread distribution of radioactive material in consumer products) should not be more than 1 mrem/yr (0.01 mSv/yr), and the collective population dose for all groups should be less than 1000 person-rem/yr (10 person-Sv/yr). (5,6)

Table 6. Dose versus risk based on the linear, nonthreshold model.

Incremental annual dose[a]	Hypothetical incremental annual risk[b]	Hypothetical lifetime risk from continuing annual dose[b]
100 mrem (1.0 mSv)	5×10^{-5}	3.5×10^{-3}
10 mrem (0.1 mSv)	5×10^{-6}	3.5×10^{-4}
1 mrem (0.01 mSv)	5×10^{-7}	3.5×10^{-5}
0.1 mrem (0.001 mSv)	5×10^{-8}	3.5×10^{-6}

[a]The expression of dose refers to the *total effective dose equivalent.* This term is the sum of the deep (whole body) dose equivalent for sources external to the body and the committed effective (whole body) dose equivalent for sources internal to the body.
[b]Calculated using a conservative risk coefficient of 5×10^{-4} per rem (5×10^{-2} per Sv) for low energy transfer radiation based on the results reported in *Sources, Effects and Risks of Ionizing Radiation,* United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 1998 Report to the General Assembly with Annexes; and *Health Effects of Exposures to Low Levels of Ionizing Radiation, BEIR V,* 1990 Committee on Biological Effects of Ionizing Radiation, National Research Council (see also NUREG/CR-4214, Rev. 1).

Table 7 shows the maximum radiological risks to the affected population from the disposal of the SLAC concrete/rebar debris at a municipal landfill. These risks were determined based on the current scientific accepted risk for low-level radiation exposure and the conservative (worst-case) dose estimates using the IMPACTS-BRC code. The risks shown are extremely low compared to other generally accepted radiological risks to individuals. For example, the risk to individuals associated with the nuclear fuel cycle is estimated to be $<6.0 \times 10^{-07}$, the risk to individuals exposed to naturally occurring radioactivity is 5.6×10^{-05}, and the risk to individuals exposed to natural radon is 1.4×10^{-03}.(7)

Table 7. Summary of maximum risk of excess fatal cancers resulting from disposal of SLAC waste.

Affected population	Calculated effective dose equivalent	Radiological risk
Transportation/handler	6.0×10^{-12} mrem/yr	3.00×10^{-08}/individual
Transportation/population	7.8×10^{-02} person-mrem/yr	3.90×10^{-08}/population
Disposal site/worker	7.4×10^{-11} mrem/yr	3.70×10^{-09}/indiv. & pop.
Disposal site/intruder	2.1×10^{-01} mrem/yr	1.05×10^{-09}/individual
Off site/individual	6.5×10^{-08} mrem/yr	3.25×10^{-14}/individual
Off site/population	3.8×10^{-06} person-mrem/yr	1.90×10^{-12}/population

CONCLUSION

Using the IMPACTS-BRC computer code, the DOE/SF calculated the potential radiological doses to maximum exposed individuals and to the general population resulting from the landfill disposal of SLAC's activated concrete/rebar debris. Using the conservative (worst-case) dose results from this analysis, a risk assessment was performed to determine the radiological impact of this operation. This assessment showed that the impact to the worker, to the public, and to the environment would be negligible by every measurement and scientific principal. The State of California, and hence the NRC, concurred with this evaluation, and has issued an exemption to proceed with the disposal of this waste at the Ox Mountain municipal landfill as BRC waste, without regard to its radioactivity (Appendix B).

REFERENCES

1. Forston, J. M., Goode, D. J., De Minimis Waste Impacts Analysis Methodology—IMPACTS-BRC Users Guide and Methodology for Radioactive Wastes Below Regulatory Concern. NUREG/CR-3585, Vol. 2, U.S. Nuclear Regulatory Commission, July, 1986. (Reports)
2. O'Neal, B. L., Lee, C. E. IMPACTS-BRC Version 2.0, Program User's Manual, NUREG/CR-5517, SAND89-3060, Sandia National Laboratories, Applied Physics, Inc. (Reports)
3. U.S. Department of Energy. Environmental Survey Preliminary Report. Stanford Linear Accelerator Center, DOE/EH/OEV-38-P, July, 1988. (Reports)
4. Oztunali, O. I., and Roles, G. W. De Minimis Waste Impacts Analysis Methodology. NUREG/CR-3585, Prepared for the U.S. Nuclear Regulatory Commission by Dames and Moore, February, 1984. (Reports)
5. U.S. Nuclear Regulatory Commission. Below Regulatory Concern Policy Statement. 55 FR 27522-37, July 3, 1990. (Regulations)
6. U.S. Nuclear Regulatory Commission Views, Chilk, S. J., Secretary of the Commission. Below Regulatory Concern; Policy Statement. June 22, 1990. (Regulations)
7. Health Effects of Exposures to Low Levels of Ionizing Radiation, BEIR V. 1990. *(Books)*

Appendix A

TABLE A-1
RADIOLOGICAL ASSESSMENT OF CONCRETE/REBAR DISPOSAL
AT THE STANFORD LINEAR ACCELERATOR CENTER
(DATA FROM SLAC)

IMPACTS-BRC - VERSION 2 0: Run on 10/13/92 at 16 35 14 50

RADIOISOTOPE INPUT PARAMETERS (μCi/g):

NA-22	D	9 490E-07	SC-46 Y 5 950E-09
MN-54	W	5 410E-07	CO-57 Y 3 730E-07
CO-60	Y	2 410E 06	

SANITARY LANDFILL

LIFE= 1 OVFL= 1 NSTR= 1
REGN= 2 DATA= 2
IPOP= 2 INST= 19

OPTIONAL ENVIRONMENTAL PARAMETERS
PRC = 1 80E-01 TXC = 1 00E+00 QFC = 1 10E+02 2 00E+05 4 50E+06
FSC = 2 64E-10 DTTM= 1 70E+00 TTM = 1 85E+00 2 50E+01 5 00E+01
FSA = 8 06E-11 DTPC= 0 00E+00 TPC = 0 00E+00 0 00E+00 0 00E+00
WVEL= 6 67E+00 AXOQ= 1 40E-10 EFAC= 7 95E-06

WASTE SLAC CONC WEIGHT 2 17E+01 Mg DENSITY 2 40E+00 Mg/m^3

ID= 2 IA= 1 IK1= 0 IK2= 0 PROCESS= 1
IXS= 1 100 0 1
ICS= 0 0 0 0

TRANSPORTATION IMPACTS
TR-MAX = 2 98E-02 mrem/y
TR-OCC = 5 97E-02 Person-mrem/y
TR-POP = 3 91E-02 Person-mrem/y

INTRUDER IMPACTS (mrem/y):

SCN	LUNGS	S WALL	LLI WALL	T BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
INT-CO	7 03E-05	7 01E-05	7 01E-05	7 01E-05	7 01E-05	7 01E-05	7 01E-05	7 01E-05	7 01E-05	7 01E-05
INT-AG	3 32E-04	3 32E-04	3 32E-04	3 32E-04	3 32E-04	3 32E-04	3 32E-04	3 32E-04	3 32E-04	3 32E-04

EXPOSED WASTE IMPACTS (mrem/y):

SCN	LUNGS	S WALL	LLI WALL	T BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
IN-AIR	1 25E-07	2 75E-08	5 46E-08	0 00E+00	2 39E-08	3 22E-08	2 50E-08	2 37E-08	2 53E-08	4 42E-08
ER-AIR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
IN-WAT	1 41E-10	1 59E-10	4 74E-10	0 00E+00	1 58E-10	1 85E-10	1 63E-10	1 60E-10	1 64E-10	2 19E-10
ER-WAT	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00

INCINERATION AND OPERATIONAL IMPACTS UNITS IC-IND,IC-MWR,OP-IND,OP-MWR - (mrem/y)
IC-POP,IC-WOR,OP-POP,OP-WOR - (Person-mrem/y)

SCN	LUNGS	S WALL	LLI WALL	T BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
IC-POP	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
IC-IND	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
IC-WOR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
IC-MWR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
OP-POP	3 58E-06	1 11E-06	1 85E-06	0 00E+00	1 02E-06	1 22E-06	1 20E-06	1 31E-06	1 05E-06	1 59E-06
OP-IND	6 19E-08	1 92E-08	3 20E-08	0 00E+00	1 76E-08	2 11E-08	2 08E-08	2 27E-08	1 82E-08	2 75E-08
OP-WOR	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03
OP-MWR	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03	4 07E-03

LEACHATE ACCUMULATION IMPACTS UNITS : LA-OPS, LA-OVF - (mrem/y); LA-AIR - (Person-mrem/y)

SCN	LUNGS	S WALL	LLI WALL	T BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
LA-OPS	5 38E-07	5 26E-07	1 68E-06	0 00E+00	5 21E-07	6 37E-07	5 29E-07	5 13E-07	5 37E-07	7 42E-07
LA-OVF	3 62E-08	4 07E-08	1 28E-07	0 00E+00	4 04E-08	4 80E-08	4 05E-08	3 87E-08	4 23E-08	5 69E-08
LA-AIR	2 00E-07	4 20E-08	8 55E-08	0 00E+00	3 62E-08	4 97E-08	3 71E-08	3 44E-08	3 86E-08	6 87E-08

GROUND WATER IMPACTS (mrem/y):

INTRUDER-WELL

TIME	LUNGS	S WALL	LLI WALL	T BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	1 52E-04	1 68E-04	5 07E-04	0 00E+00	1 68E-04	1 97E-04	1 69E-04	1 62E-04	1 79E-04	2 34E-04
40YR	1 07E-05	1 19E-05	3 58E-05	0 00E+00	1 19E-05	1 39E-05	1 19E-05	1 15E-05	1 26E-05	1 65E-05
60YR	7 59E-07	8 42E-07	2 53E-06	0 00E+00	8 40E-07	9 85E-07	8 43E-07	8 11E-07	8 92E-07	1 17E-06
80YR	5 36E-08	5 95E-08	1 79E-07	0 00E+00	5 94E-08	6 96E-08	5 96E-08	5 74E-08	6 31E-08	8 26E-08
100YR	3 79E-09	4 21E-09	1 27E-08	0 00E+00	4 20E-09	4 92E-09	4 22E-09	4 06E-09	4 46E-09	5 84E-09
120YR	2 68E-10	2 98E-10	8 95E-10	0 00E+00	2 97E-10	3 48E-10	2 98E-10	2 87E-10	3 15E-10	4 13E-10
160YR	1 34E-12	1 49E-12	4 48E-12	0 00E+00	1 49E-12	1 74E-12	1 49E-12	1 43E-12	1 58E-12	2 07E-12
200YR	6 71E-15	7 44E-15	2 24E-14	0 00E+00	7 43E-15	8 71E-15	7 46E-15	7 17E-15	7 89E-15	1 03E-14
400YR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
600YR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
800YR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
1K YR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
2K YR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
5K YR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
10K YR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00
20K YR	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00	0 00E+00

POPULATION-WELL

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
40YR	4.40E-08	4.88E-08	1.47E-07	0.00E+00	4.87E-08	5.71E-08	4.89E-08	4.70E-08	5.17E-08	6.77E-08
60YR	3.46E-09	3.83E-09	1.15E-08	0.00E+00	3.83E-09	4.49E-09	3.84E-09	3.70E-09	4.06E-09	5.32E-09
80YR	2.44E-10	2.71E-10	8.16E-10	0.00E+00	2.71E-10	3.17E-10	2.72E-10	2.61E-10	2.87E-10	3.76E-10
100YR	1.73E-11	1.92E-11	5.77E-11	0.00E+00	1.91E-11	2.24E-11	1.92E-11	1.85E-11	2.03E-11	2.66E-11
120YR	1.22E-12	1.36E-12	4.08E-12	0.00E+00	1.35E-12	1.59E-12	1.36E-12	1.31E-12	1.44E-12	1.88E-12
160YR	6.11E-15	6.78E-15	2.04E-14	0.00E+00	6.77E-15	7.93E-15	6.79E-15	6.53E-15	7.19E-15	9.41E-15
200YR	3.06E-17	3.39E-17	1.02E-16	0.00E+00	3.38E-17	3.97E-17	3.40E-17	3.27E-17	3.59E-17	4.71E-17
400YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
600YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
800YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

POPULATION-SURFACE WATER

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
40YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
60YR	9.41E-11	1.06E-10	3.33E-10	0.00E+00	1.05E-10	1.25E-10	1.05E-10	1.01E-10	1.10E-10	1.48E-10
80YR	1.11E-11	1.25E-11	3.92E-11	0.00E+00	1.24E-11	1.47E-11	1.24E-11	1.19E-11	1.30E-11	1.75E-11
100YR	7.85E-13	8.83E-13	2.77E-12	0.00E+00	8.76E-13	1.04E-12	8.79E-13	8.39E-13	9.18E-13	1.23E-12
120YR	5.55E-14	6.24E-14	1.96E-13	0.00E+00	6.20E-14	7.36E-14	6.21E-14	5.93E-14	6.49E-14	8.73E-14
160YR	2.77E-16	3.12E-16	9.81E-16	0.00E+00	3.10E-16	3.68E-16	3.11E-16	2.97E-16	3.25E-16	4.37E-16
200YR	1.39E-18	1.56E-18	4.90E-18	0.00E+00	1.55E-18	1.84E-18	1.55E-18	1.48E-18	1.62E-18	2.18E-18
400YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
600YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
800YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

SANITARY LANDFILL

LIFE= 1 OVFL= 1 NSTR= 1
REGN= 2 DATA= 2 IPOP= 2 INST= 19

OPTIONAL ENVIRONMENTAL PARAMETERS
PRC = 1.80E-01 TXC = 1.00E+00 QFC = 1.10E+02 2.00E+05 4.50E+06
FSC = 2.64E-10 DTTM= 1.70E+00 TTM = 1.85E+00 2.50E+01 5.00E+01
FSA = 8.06E-11 DTPC= 0.00E+00 TPC = 0.00E+00 0.00E+00 0.00E+00
WVEL= 6.67E+00 AXOQ= 1.40E-10 EFAC= 7.95E-06

WASTE: SLAC REBAR WEIGHT: 2.30E+00 Mg DENSITY: 7.85E+00 Mg/m^3

ID= 2 IA= 2 IK1= 0 IK2= 0 PROCESS= 1
IXS= 1 100 0 1 ICS= 0 100 0 0

TRANSPORTATION IMPACTS
TR-MAX = 3.16E-03 mrem/y
TR-OCC = 6.33E-03 Person-mrem/y
TR-POP = 4.15E-03 Person-mrem/y

INTRUDER IMPACTS (mrem/y):

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
INT-CO	7.45E-07	7.43E-07	7.43E-07	7.43E-07	7.43E-07	7.43E-07	7.43E-07	7.43E-07	7.43E-07	7.43E-07
INT-AG	3.52E-06	3.52E-06	3.52E-06	3.52E-06	3.52E-06	3.52E-06	3.52E-06	3.52E-06	3.52E-06	3.52E-06

EXPOSED WASTE IMPACTS (mrem/y):

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
IN-AIR	1.33E-09	2.91E-10	5.78E-10	0.00E+00	2.53E-10	3.41E-10	2.65E-10	2.51E-10	2.69E-10	4.69E-10
ER-AIR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IN-WAT	1.50E-12	1.68E-12	5.03E-12	0.00E+00	1.67E-12	1.96E-12	1.72E-12	1.70E-12	1.74E-12	2.32E-12
ER-WAT	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

INCINERATION AND OPERATIONAL IMPACTS: UNITS: IC-IND,IC-MWR,OP-IND,OP-MWR - (mrem/y)
IC-POP,IC-WOR,OP-POP,OP-WOR - (Person-mrem/y)

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
IC-POP	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IC-IND	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00,
IC-WOR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IC-MWR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
OP-POP	3.79E-07	1.18E-07	1.96E-07	0.00E+00	1.08E-07	1.29E-07	1.27E-07	1.39E-07	1.12E-07	1.68E-07
OP-IND	6.56E-09	2.04E-09	3.39E-09	0.00E+00	1.87E-09	2.24E-09	2.20E-09	2.40E-09	1.93E-09	2.91E-09
OP-WOR	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05
OP-MWR	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05	4.32E-05

LEACHATE ACCUMULATION IMPACTS UNITS : LA-OPS, LA-OVF - (mrem/y), LA-AIR - (Person mrem/y)

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
LA-OPS	5.70E-09	5.58E-09	1.78E-08	0.00E+00	5.52E-09	6.75E-09	5.61E-09	5.44E-09	5.69E-09	7.86E-09
LA-OVF	3.83E-10	4.31E-10	1.35E-09	0.00E+00	4.28E-10	5.09E-10	4.29E-10	4.10E-10	4.48E-10	6.03E-10
LA-AIR	2.12E-09	4.45E-10	9.06E-10	0.00E+00	3.84E-10	5.26E-10	3.94E-10	3.65E-10	4.09E-10	7.28E-10

GROUND WATER IMPACTS (mrem/y):

INTRUDER-WELL

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	1.62E-06	1.80E-06	5.41E-06	0.00E+00	1.80E-06	2.11E-06	1.80E-06	1.74E-06	1.91E-06	2.50E-06
40YR	1.16E-07	1.28E-07	3.86E-07	0.00E+00	1.28E-07	1.50E-07	1.29E-07	1.24E-07	1.36E-07	1.78E-07
60YR	8.24E-09	9.14E-09	2.75E-08	0.00E+00	9.13E-09	1.07E-08	9.16E-09	8.81E-09	9.69E-09	1.27E-08
80YR	5.88E-10	6.52E-10	1.96E-09	0.00E+00	6.51E-10	7.63E-10	6.53E-10	6.28E-10	6.91E-10	9.05E-10
100YR	4.19E-11	4.65E-11	1.40E-10	0.00E+00	4.64E-11	5.44E-11	4.66E-11	4.48E-11	4.93E-11	6.45E-11
120YR	2.99E-12	3.31E-12	9.97E-12	0.00E+00	3.31E-12	3.88E-12	3.32E-12	3.19E-12	3.51E-12	4.60E-12
160YR	1.52E-14	1.68E-14	5.07E-14	0.00E+00	1.68E-14	1.97E-14	1.69E-14	1.62E-14	1.79E-14	2.34E-14
200YR	7.72E-17	8.56E-17	2.58E-16	0.00E+00	8.55E-17	1.00E-16	8.58E-17	8.25E-17	9.07E-17	1.19E-16
400YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
600YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
800YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

POPULATION-WELL

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
40YR	4.74E-10	5.26E-10	1.58E-09	0.00E+00	5.25E-10	6.15E-10	5.27E-10	5.07E-10	5.57E-10	7.30E-10
60YR	3.75E-11	4.17E-11	1.25E-10	0.00E+00	4.16E-11	4.87E-11	4.17E-11	4.01E-11	4.41E-11	5.78E-11
80YR	2.68E-12	2.97E-12	8.93E-12	0.00E+00	2.96E-12	3.47E-12	2.98E-12	2.86E-12	3.15E-12	4.12E-12
100YR	1.91E-13	2.12E-13	6.37E-13	0.00E+00	2.11E-13	2.48E-13	2.12E-13	2.04E-13	2.24E-13	2.94E-13
120YR	1.36E-14	1.51E-14	4.54E-14	0.00E+00	1.51E-14	1.77E-14	1.51E-14	1.45E-14	1.60E-14	2.10E-14
160YR	6.92E-17	7.67E-17	2.31E-16	0.00E+00	7.66E-17	8.98E-17	7.69E-17	7.40E-17	8.13E-17	1.07E-16
200YR	3.52E-19	3.90E-19	1.17E-18	0.00E+00	3.89E-19	4.56E-19	3.91E-19	3.76E-19	4.13E-19	5.41E-19
400YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
600YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
800YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

POPULATION-SURFACE WATER

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
40YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
60YR	1.02E-12	1.15E-12	3.61E-12	0.00E+00	1.14E-12	1.36E-12	1.15E-12	1.09E-12	1.20E-12	1.61E-12
80YR	1.22E-13	1.37E-13	4.30E-13	0.00E+00	1.36E-13	1.61E-13	1.36E-13	1.30E-13	1.42E-13	1.91E-13
100YR	8.66E-15	9.75E-15	3.06E-14	0.00E+00	9.68E-15	1.15E-14	9.70E-15	9.26E-15	1.01E-14	1.36E-14
120YR	6.18E-16	6.95E-16	2.18E-15	0.00E+00	6.90E-16	8.20E-16	6.92E-16	6.61E-16	7.23E-16	9.72E-16
160YR	3.14E-18	3.53E-18	1.11E-17	0.00E+00	3.51E-18	4.17E-18	3.52E-18	3.36E-18	3.67E-18	4.94E-18
200YR	1.60E-20	1.80E-20	5.64E-20	0.00E+00	1.78E-20	2.12E-20	1.79E-20	1.71E-20	1.87E-20	2.51E-20
400YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
600YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
800YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Total Run Time = 0.1080 Minute(s)

Appendix B

TABLE A-2
RADIOLOGICAL ASSESSMENT OF CONCRETE/REBAR DISPOSAL
AT THE STANFORD LINEAR ACCELERATOR CENTER
(DATA FROM LLNL)

IMPACTS-BRC - VERSION 2.0. Run on 10/16/92 at 15:50:49.07

RADIONUCLIDE INPUT PARAMETERS (μCi/g):

CONCRETE DEBRIS

NA-22	D	9.040E-07	ZN-65	Y	7.667E-08
SC-46	Y	2.000E-08	CS-134	D	5.000E-08
MN-54	W	1.346E-06	EU-152	W	1.290E-06
CO-57	Y	4.333E-08	EU-154	W	1.475E-07
CO-60	Y	2.626E-06			

REBAR/WIRE ANALYSIS

MN-54	W	3.067E-06
CO-57	Y	1.280E-06
CO-60	Y	5.467E-06

SANITARY LANDFILL

LIFE= 1 OVFL= 1 MSTR= 1
REGN= 2 DATA= 2
IPOP= 2 INST= 19

OPTIONAL ENVIRONMENTAL PARAMETERS
PRC = 1.80E-01 TXC = 1.00E+00 QFC = 1.10E+02 2.00E+05 4.50E+06
FSC = 2.64E-10 DTTM= 1.70E+00 TTM = 1.85E+00 2.50E+01 5.00E+01
FSA = 8.06E-11 DTPC= 0.00E+00 TPC = 0.00E+00 0.00E+00 0.00E+00
WVEL= 6.67E+00 AXOQ= 1.40E-10 EFAC= 7.95E-06

WASTE: CONC/LLNL WEIGHT: 2.17E+01 Mg DENSITY: 2.40E+00 Mg/M3
ID= 2 IA= 1 IK1= 0 IK2= 0 PROCESS= 1
IXS= 1 100 0 1 ICS= 0 0 0 0

TRANSPORTATION IMPACTS

TR-MAX = 5.37E-02 mrem/y
TR-OCC = 1.07E-01 Person-mrem/y
TR-POP = 7.04E-02 Person-mrem/y

INTRUDER IMPACTS (mrem/y):

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
INT-CO	3.58E-04	3.57E-04	3.57E-04	3.57E-04	3.57E-04	3.59E-04	3.58E-04	3.58E-04	3.57E-04	3.58E-04
INT-AG	1.69E-03	1.69E-03	1.69E-03	1.69E-03	1.69E-03	1.69E-03	1.69E-03	1.69E-03	1.69E-03	1.69E-03

EXPOSED WASTE IMPACTS (mrem/y):

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
IN-AIR	3.72E-07	1.60E-07	4.44E-07	0.00E+00	2.05E-07	1.19E-06	3.46E-07	8.85E-07	1.27E-07	3.41E-07
ER-AIR	4.18E-28	1.86E-28	8.50E-28	0.00E+00	2.42E-28	1.96E-27	5.62E-28	2.40E-27	1.43E-28	5.14E-28
IN-WAT	6.85E-10	7.93E-10	4.07E-09	0.00E+00	7.69E-10	1.56E-09	9.16E-10	1.36E-09	7.80E-10	1.30E-09
ER-WAT	4.24E-29	5.33E-29	4.46E-28	0.00E+00	4.73E-29	1.20E-28	6.37E-29	1.44E-28	4.86E-29	1.02E-28

INCINERATION AND OPERATIONAL IMPACTS: UNITS: IC-IND,IC-MWR,OP-IND,OP-MWR - (mrem/y)
IC-POP,IC-WOR,OP-POP,OP-WOR - (Person mrem/y)

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
IC-POP	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IC-IND	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IC-WOR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IC-MWR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
OP-POP	5.35E-06	2.02E-06	4.30E-06	0.00E+00	2.20E-06	7.99E-06	3.17E-06	6.71E-06	1.79E-06	3.47E-06
OP-IND	9.26E-08	3.49E-08	7.45E-08	0.00E+00	3.82E-08	1.38E-07	5.49E-08	1.16E-07	3.10E-08	6.01E-08
OP-WOR	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03
OP-MWR	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03	7.33E-03

LEACHATE ACCUMULATION IMPACTS UNITS : LA-OPS, LA-OVF - (mrem/y), LA-AIR - (Person-mrem/y)

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
LA-OPS	7.90E-07	6.89E-07	2.08E-06	0.00E+00	6.95E-07	8.52E-07	7.26E-07	1.78E-06	6.84E-07	9.55E-07
LA-OVF	4.05E-08	4.56E-08	1.47E-07	0.00E+00	4.52E-08	5.51E-08	4.57E-08	4.46E-08	4.73E-08	6.42E-08
LA-AIR	2.20E-07	4.73E-08	9.77E-08	0.00E+00	4.16E-08	6.81E-08	4.43E-08	4.78E-08	4.33E-08	7.84E-08

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GROUND WATER IMPACTS (mrem/y):

INTRUDER-WELL

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	1.66E-04	1.84E-04	5.55E-04	0.00E+00	1.84E-04	2.16E-04	1.85E-04	1.78E-04	1.95E-04	2.56E-04
40YR	1.20E-05	1.34E-05	4.09E-05	0.00E+00	1.33E-05	1.59E-05	1.34E-05	1.32E-05	1.41E-05	1.86E-05
60YR	9.99E-07	1.11E-06	3.74E-06	0.00E+00	1.11E-06	1.46E-06	1.15E-06	1.24E-06	1.17E-06	1.59E-06
80YR	1.57E-07	1.75E-07	7.58E-07	0.00E+00	1.73E-07	2.98E-07	1.95E-07	2.65E-07	1.82E-07	2.72E-07
100YR	4.43E-08	4.98E-08	2.47E-07	0.00E+00	4.88E-08	9.64E-08	5.79E-08	8.82E-08	5.14E-08	8.14E-08
120YR	1.64E-08	1.85E-08	9.52E-08	0.00E+00	1.80E-08	3.69E-08	2.17E-08	3.42E-08	1.90E-08	3.06E-08
160YR	2.75E-09	3.11E-09	1.66E-08	0.00E+00	3.03E-09	6.27E-09	3.66E-09	5.93E-09	3.18E-09	5.20E-09
200YR	3.38E-10	3.84E-10	2.11E-09	0.00E+00	3.72E-10	7.77E-10	4.52E-10	7.52E-10	3.92E-10	6.47E-10
400YR	1.83E-14	2.15E-14	1.45E-13	0.00E+00	2.00E-14	4.42E-14	2.54E-14	4.99E-14	2.13E-14	3.81E-14
600YR	2.44E-18	2.92E-18	2.10E-17	0.00E+00	2.67E-18	6.03E-18	3.44E-18	7.18E-18	2.85E-18	5.26E-18
800YR	4.10E-22	4.90E-22	3.57E-21	0.00E+00	4.48E-22	1.02E-21	5.78E-22	1.22E-21	4.79E-22	8.88E-22
1K YR	7.08E-26	8.47E-26	6.18E-25	0.00E+00	7.74E-26	1.75E-25	9.98E-26	2.11E-25	8.28E-26	1.53E-25
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

POPULATION-WELL

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
40YR	4.79E-08	5.32E-08	1.60E-07	0.00E+00	5.31E-08	6.22E-08	5.33E-08	5.13E-08	5.64E-08	7.38E-08
60YR	3.77E-09	4.18E-09	1.26E-08	0.00E+00	4.17E-09	4.89E-09	4.19E-09	4.03E-09	4.43E-09	5.80E-09
80YR	2.66E-10	2.95E-10	8.89E-10	0.00E+00	2.95E-10	3.46E-10	2.96E-10	2.85E-10	3.13E-10	4.10E-10
100YR	1.88E-11	2.09E-11	6.29E-11	0.00E+00	2.09E-11	2.44E-11	2.09E-11	2.01E-11	2.21E-11	2.90E-11
120YR	1.33E-12	1.48E-12	4.44E-12	0.00E+00	1.47E-12	1.73E-12	1.48E-12	1.42E-12	1.57E-12	2.05E-12
160YR	6.66E-15	7.39E-15	2.22E-14	0.00E+00	7.37E-15	8.64E-15	7.40E-15	7.12E-15	7.83E-15	1.03E-14
200YR	3.33E-17	3.69E-17	1.11E-16	0.00E+00	3.69E-17	4.32E-17	3.70E-17	3.56E-17	3.91E-17	5.13E-17
400YR	8.34E-17	9.81E-17	6.59E-16	0.00E+00	9.13E-17	2.02E-16	1.16E-16	2.27E-16	9.72E-17	1.74E-16
600YR	1.11E-20	1.33E-20	9.59E-20	0.00E+00	1.22E-20	2.75E-20	1.56E-20	3.27E-20	1.30E-20	2.40E-20
800YR	1.87E-24	2.23E-24	1.63E-23	0.00E+00	2.04E-24	4.63E-24	2.63E-24	5.55E-24	2.18E-24	4.04E-24
1K YR	3.22E-28	3.86E-28	2.81E-27	0.00E+00	3.53E-28	7.99E-28	4.55E-28	9.59E-28	3.77E-28	6.99E-28
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

POPULATION-SURFACE WATER

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
40YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
60YR	1.03E-10	1.15E-10	3.63E-10	0.00E+00	1.15E-10	1.36E-10	1.15E-10	1.10E-10	1.20E-10	1.61E-10
80YR	1.21E-11	1.36E-11	4.27E-11	0.00E+00	1.35E-11	1.60E-11	1.35E-11	1.29E-11	1.41E-11	1.90E-11
100YR	8.55E-13	9.62E-13	3.02E-12	0.00E+00	9.55E-13	1.13E-12	9.58E-13	9.14E-13	1.00E-12	1.35E-12
120YR	6.05E-14	6.80E-14	2.14E-13	0.00E+00	6.75E-14	8.02E-14	6.77E-14	6.46E-14	7.07E-14	9.52E-14
160YR	3.02E-16	3.40E-16	1.07E-15	0.00E+00	3.38E-16	4.01E-16	3.39E-16	3.23E-16	3.54E-16	4.76E-16
200YR	1.51E-18	1.70E-18	5.34E-18	0.00E+00	1.69E-18	2.01E-18	1.69E-18	1.62E-18	1.77E-18	2.38E-18
400YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
600YR	5.07E-22	6.37E-22	5.27E-21	0.00E+00	5.67E-22	1.43E-21	7.60E-22	1.70E-21	5.81E-22	1.21E-21
800YR	8.51E-26	1.07E-25	8.95E-25	0.00E+00	9.51E-26	2.41E-25	1.28E-25	2.89E-25	9.76E-26	2.04E-25
1K YR	1.47E-29	1.85E-29	1.55E-28	0.00E+00	1.64E-29	4.16E-29	2.21E-29	5.00E-29	1.68E-29	3.53E-29
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

SANITARY LANDFILL

LIFE= 1 OVFL= 1 NSTR= 1
REGN= 2 DATA= 2
IPOP= 2 INST= 19

OPTIONAL ENVIRONMENTAL PARAMETERS
PRC = 1.80E-01 TXC = 1.00E+00 QFC = 1.10E+02 2.00E+05 4.50E+06
FSC = 2.64E-10 DTTM= 1.70E+00 TTH = 1.85E+00 2.50E+01 5.00E+01
FSA = 8.06E-11 DTPC= 0.00E+00 TPC = 0.00E+00 0.00E+00 0.00E+00
WVEL= 6.67E+00 AXOQ= 1.40E-10 EFAC= 7.95E-06

WASTE: REBAR-LLNL WEIGHT: 2.30E+00 Mg DENSITY: 7.85E+00 Mg/M3

ID= 2 IA= 2 IK1= 0 IK2= 0 PROCESS= 1
IXS= 1 100 0 1
ICS= 0 100 0 0

TRANSPORTATION IMPACTS

TR-MAX = 5.97E-03 mrem/y
TR-OCC = 1.19E-02 Person-mrem/y
TR-POP = 7.82E-03 Person-mrem/y

INTRUDER IMPACTS (mrem/y):

SCN	LUNGS	S WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
INT-CO	1.64E-06	1.64E-06	1.64E-06	1.64E-06	1.64E-06	1.64E-06	1.64E-06	1.64E-06	1.64E-06	1.64E 06
INT-AG	7.76E-06	7.76E-06	7.76E-06	7.76E-06	7.76E-06	7.76E-06	7.76E-06	7.76E-06	7.76E-06	7.76E-06

EXPOSED WASTE IMPACTS (mrem/y):

SCN	LUNGS	S WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
IN-AIR	2.99E-09	6.28E-10	1.28E-09	0.00E+00	5.41E-10	7.42E-10	5.55E-10	5.14E-10	5.77E-10	1.03E-09
ER-AIR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IN-WAT	3.14E-12	3.54E-12	1.11E-11	0.00E+00	3.51E-12	4.17E-12	3.52E-12	3.36E-12	3.68E-12	4.95E-12
ER-WAT	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

INCINERATION AND OPERATIONAL IMPACTS: UNITS: IC-IND,IC-MWR,OP-IND,OP-MWR - (mrem/y)
IC-POP,IC-WOR,OP-POP,OP-WOR - (Person-mrem/y)

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
IC-POP	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IC-IND	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IC-WOR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
IC-MWR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
OP-POP	7.96E-07	1.78E-07	3.63E-07	0.00E+00	1.56E-07	2.14E-07	1.62E-07	1.54E-07	1.67E-07	2.86E-07
OP-IND	1.38E-08	3.07E-09	6.28E-09	0.00E+00	2.70E-09	3.70E-09	2.80E-09	2.67E-09	2.89E-09	4.95E-09
OP-WOR	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05
OP-MWR	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05	8.14E-05

LEACHATE ACCUMULATION IMPACTS UNITS : LA-OPS, LA-OVF (mrem/y): LA-AIR - (Person-mrem/y)

SCN	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
LA-OPS	1.60E-08	1.32E-08	4.36E-08	0.00E+00	1.30E-08	1.66E-08	1.33E-08	1.30E-08	1.31E-08	1.89E-08
LA-OVF	8.69E-10	9.77E-10	3.07E-09	0.00E+00	9.70E-10	1.15E-09	9.73E-10	9.29E-10	1.02E-09	1.37E-09
LA-AIR	4.80E-09	1.01E-09	2.05E-09	0.00E+00	8.70E-10	1.19E-09	8.92E-10	8.26E-10	9.27E-10	1.65E-09

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GROUND WATER IMPACTS (mrem/y):

INTRUDER-WELL

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	3.68E-06	4.08E-06	1.23E-05	0.00E+00	4.07E-06	4.77E-06	4.09E-06	3.93E-06	4.32E-06	5.66E-06
40YR	2.62E-07	2.91E-07	8.75E-07	0.00E+00	2.90E-07	3.40E-07	2.92E-07	2.80E-07	3.08E-07	4.04E-07
60YR	1.87E-08	2.07E-08	6.24E-08	0.00E+00	2.07E-08	2.43E-08	2.08E-08	2.00E-08	2.20E-08	2.88E-08
80YR	1.33E-09	1.48E-09	4.45E-09	0.00E+00	1.48E-09	1.73E-09	1.48E-09	1.43E-09	1.57E-09	2.05E-09
100YR	9.50E-11	1.05E-10	3.17E-10	0.00E+00	1.05E-10	1.23E-10	1.06E-10	1.02E-10	1.12E-10	1.46E-10
120YR	6.78E-12	7.52E-12	2.26E-11	0.00E+00	7.50E-12	8.80E-12	7.53E-12	7.24E-12	7.97E-12	1.04E-11
160YR	3.44E-14	3.82E-14	1.15E-13	0.00E+00	3.81E-14	4.47E-14	3.83E-14	3.68E-14	4.05E-14	5.30E-14
200YR	1.75E-16	1.94E-16	5.84E-16	0.00E+00	1.94E-16	2.27E-16	1.95E-16	1.87E-16	2.06E-16	2.70E-16
400YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
600YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
800YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

POPULATION-WELL

TIME	LUNGS	S.WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
40YR	1.08E-09	1.19E-09	3.59E-09	0.00E+00	1.19E-09	1.40E-09	1.20E-09	1.15E-09	1.26E-09	1.66E-09
60YR	8.52E-11	9.45E-11	2.84E-10	0.00E+00	9.43E-11	1.11E-10	9.47E-11	9.11E-11	1.00E-10	1.31E-10
80YR	6.07E-12	6.74E-12	2.03E-11	0.00E+00	6.72E-12	7.88E-12	6.75E-12	6.49E-12	7.14E-12	9.35E-12
100YR	4.33E-13	4.80E-13	1.44E-12	0.00E+00	4.79E-13	5.62E-13	4.81E-13	4.63E-13	5.09E-13	6.67E-13
120YR	3.09E-14	3.42E-14	1.03E-13	0.00E+00	3.42E-14	4.01E-14	3.43E-14	3.30E-14	3.63E-14	4.75E-14
160YR	1.57E-16	1.74E-16	5.24E-16	0.00E+00	1.74E-16	2.04E-16	1.74E-16	1.68E-16	1.84E-16	2.42E-16
200YR	7.97E-19	8.85E-19	2.66E-18	0.00E+00	8.83E-19	1.04E-18	8.87E-19	8.53E-19	9.38E-19	1.23E-18
400YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
600YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
800YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

POPULATION-SURFACE WATER

TIME	LUNGS	S WALL	LLI WALL	T. BODY	KIDNEYS	LIVER	RED MAR	BONE	THYROID	ICRP
20YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
40YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
60YR	2.32E-12	2.61E-12	8.20E-12	0.00E+00	2.59E-12	3.08E-12	2.60E-12	2.48E-12	2.71E-12	3.65E-12
80YR	2.76E-13	3.10E-13	9.74E-13	0.00E+00	3.08E-13	3.66E-13	3.09E-13	2.95E-13	3.23E-13	4.34E-13
100YR	1.97E-14	2.21E-14	6.95E-14	0.00E+00	2.19E-14	2.61E-14	2.20E-14	2.10E-14	2.30E-14	3.09E-14
120YR	1.40E-15	1.58E-15	4.95E-15	0.00E+00	1.56E-15	1.86E-15	1.57E-15	1.50E-15	1.64E-15	2.21E-15
160YR	7.12E-18	8.01E-18	2.52E-17	0.00E+00	7.95E-18	9.45E-18	7.98E-18	7.62E-18	8.33E-18	1.12E-17
200YR	3.62E-20	4.07E-20	1.28E-19	0.00E+00	4.04E-20	4.80E-20	4.06E-20	3.87E-20	4.24E-20	5.70E-20
400YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
600YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
800YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20K YR	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

CHAPTER 7

Thermal Technologies

CRITICAL OPERATING PARAMETERS FOR MICROWAVE SOLIDIFICATION OF HYDROXIDE SLUDGE

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ABSTRACT. Engineers at the Rocky Flats Plant (RFP) have developed an innovative technology for the treatment of homogeneous wet or dry solids which are contaminated with hazardous and/or radioactive materials. The process uses microwave energy to heat and melt the waste into a vitreous final form that is suitable for land disposal. The advantages include a high density, leach resistant, robust waste form; volume and toxicity reduction; favorable economics; in-container treatment; good public acceptance; isolated equipment; and instantaneous energy control. Regulatory certification of the final form is accomplished by meeting the limitation specified in U.S. Environmental Protection Agency's's Toxicity Characteristic Leach Procedure. This paper presents the results from a series of tests performed on a surrogate hydroxide coprecipitation sludge spiked with heavy metals at elevated concentrations. The results are very encouraging and support RFP's commitment to the use of microwave technology for treatment of various waste streams.

INTRODUCTION

Microwave technology has been used in the food and chemical industries since early 1970 (1). The majority of this work has been concentrated in the areas of food preparation and in the chemical industry for the vulcanization of rubber. High temperature technology was developed by the Japanese for converting plutonium nitrate, recovered from spent fuel reprocessing, to plutonium oxide for nuclear fuel and for solidifying waste incinerator ash. Laboratory scale vitrification of calcined high-level nuclear wastes using microwave energy was done by the Idaho National Engineering Laboratory in 1979. Significant work with solidification of sludges has been performed at the Rocky Flats Plant (RFP) since 1986. Hydroxide precipitation sludge is successfully being processed using a demonstration scale system. Other wastes that passed preliminary screening tests using a bench scale system include Fluidized Bed Incineration (FBI) ashes, nitrate salts, and soils. The FBI ashes included chromium oxide catalyst and ash from shredded HEPA filters. Nitrate salts were solidified by heating them to their melting points forming a salt cake (2).

The waste form produced from the process will be disposed at a Department of Energy burial site, either the Waste Isolation and Pilot Plant of the Nevada Test Site, and therefore must meet the waste acceptance criteria (WAC) for these facilities. The WAC typically requires that the waste form pass the Toxicity Characteristic Leach Procedure (TCLP) limitations as required by the Resource Conservation and Recovery Act for land disposal. In order to (a) certify that the waste form meets these requirements and (b) establish rough operating parameters for the process, wastes must be processed through the proposed treatment system and the products analyzed using TCLP methods.

The RFP microwave project team is currently optimizing the operating parameters for the full-scale (production) system to treat hydroxide coprecipitation sludge from the liquid waste treatment facilities at RFP. An experimental matrix was developed with the assistance of the RFP Statistical Applications group to identify the critical parameters for the treatment of this sludge and to provide a first estimate of their optimal value. This paper summarizes the results of these tests.

EXPERIMENTAL PROCEDURE

Surrogate wastes were produced to simulate the bulk physical and chemical properties of the hydroxide coprecipitation sludge from the RFP liquid waste treatment facilities and were processed through a bench-scale microwave system. The sludge had a per batch composition of 967 g $CaSO_4x2H_2O$, 777 g $Fe(OH)_3$, 317 g $Mg(OH)_2$, 237 g $NaNO_3$, and 207 g diatomaceous earth (filter aid). The sludge was spiked with U.S. Environmental Protection Agency (EPA) regulated heavy metals at elevated levels, refer to table 1, to evaluate the impact of various operational parameters on the TCLP leach resistance of the final waste form.

Table 1. Metal Concentrations in ppm for Actual Versus Surrogate Sludges

	Surrogate Sludge	Actual Sludge[4]
Chromium	500	54 to 481
Nickel	500	no data
Lead	500	29 to 250
Cadmium	500	4.6 to 13.0
Silver	500	56 to 189

The following operating parameters were controlled during the experimental test runs:

- Frit Composition (B/D) -- weight percent ratio of borax to diatomaceous earth (diatomite) in the frit feed.
- Waste Loading (S/F) -- weight percent ratio of waste sludge surrogate to the frit fed to the melt chamber.
- Temperature (°C) -- measured with an infrared thermometer or a thermocouple.
- Quench rate -- the speed at which the temperature of the molten material is reduced after processing.

Minimum, nominal, and maximum values for each of the operating parameters were selected. A statistical design of experiment matrix was generated specifying the values of the various operational parameters for a series of test runs. An L_{16} orthogonal array was used, placing operating parameters in columns 1, 2, 4, and 8, while centering parameter values were placed in the 4.5 and 12.5 row locations. The test matrix is contained in Table 2.

The final waste forms produced from these test runs were prepared for TCLP analyses according to EPA protocols. The solidified material was removed from the melting container and fractured using a hammer and chisel to collect a representative sample. The particle size of the samples was further reduced by placing the samples in a vice and applying pressure, thereby fracturing the samples. This preparation method was intended to reduce the amount of fine particles generated during the size reduction operation. The fines generated during the sampling and preparation operations were collected and measured to determine the weight percentage of fines.

When preparing the final 50 g subsample for extraction, the proper percentage of fines was included. According to the pH testing procedure, TCLP Fluid #1 was determined to be the proper extraction fluid for all of the samples. The 50 g subsamples were extracted and filtered as required in the TCLP protocol. The resulting leachates were digested and analyzed for the spiked metals using a Leeman Labs Plasma Spec inductively coupled plasma atomic emission spectrophotometer system.

Table 2. Test Matrix for Microwave Solidification of Surrogate Hydroxide Coprecipitation Sludge

Run No.	Frit Comp B/D	Waste Load S/F	Temperature °C	Quench Rate
1	20/80	25/75	950	slow
2	20/80	25/75	950	fast
3	20/80	25/75	1200	slow
4	20/80	25/75	1200	fast
4.5	30/70	50/50	1075	medium
5	20/80	75/25	950	slow
6	20/80	75/25	950	fast
7	20/80	75/25	1200	slow
8	20/80	75/25	1200	fast
9	40/60	25/75	950	slow
10	40/60	25/75	950	fast
11	40/60	25/75	1200	slow
12	40/60	25/75	1200	fast
12.5	30/70	50/50	1075	medium
13	40/60	75/25	950	slow
14	40/60	75/25	950	fast
15	40/60	75/25	1200	slow
16	40/60	75/25	1200	fast

Table 3. TCLP Results from Microwave Solidified Surrogate Hydroxide Coprecipitation Sludge

	Metal Concentration in ppm				
Run No.	Chromium	Nickel	Lead	Cadmium	Silver
1	0.070	0.046	0.030	0.150	ND
2	0.059	0.045	0.047	0.109	0.003
3	0.053	0.043	ND	0.092	ND
4	0.055	0.049	0.105	0.147	ND
4.5	0.072	0.039	0.219	0.339	ND
5	0.034	0.075	1.23	2.18	0.011
6	0.036	0.146	1.30	2.74	0.309
7	0.055	0.063	1.02	2.15	0.003
8	0.021	0.144	1.39	3.52	0.062
9	0.072	0.132	0.122	1.64	ND
10	0.049	0.105	0.058	0.470	0.022
11	0.044	0.106	0.070	0.295	0.015
12	0.054	0.100	0.007	0.228	0.037
12.5	0.044	0.105	0.284	1.06	0.205
13	0.380	0.173	0.059	1.63	0.135
14	0.273	0.376	1.63	3.92	0.150
15	0.054	0.277	1.61	4.52	0.202
16	ND	0.127	0.182	3.81	0.112

ND -- Not Detected.

Table 4. Impact of Operating Parameter on TCLP Results for Microwave Solidified Surrogate Sludge

Operating Parameter	Metal Concentrations in ppm Chromium	Nickel	Lead	Cadmium	Silver
Frit Comp, B/D					
20/80	0.048	0.076	0.640	1.39	0.049
30/70	0.058	0.072	0.251	0.700	0.103
40/60	0.116	0.175	0.467	2.06	0.084
Waste Load, S/F					
25/75	0.057	0.078	0.055	0.391	0.009
50/50	0.058	0.072	0.251	0.700	0.103
75/25	0.107	0.173	1.05	3.06	0.123
Temperature, °C					
950	0.123	0.137	0.560	1.60	0.079
1075	0.058	0.072	0.251	0.700	0.103
1200	0.042	0.114	0.548	1.85	0.054
Quench Rate					
slow	0.095	0.114	0.518	1.58	0.046
medium	0.058	0.072	0.251	0.700	0.103
fast	0.068	0.137	0.590	1.87	0.087

RESULTS AND DISCUSSION

The results of the TCLP analyses are contained in Table III. Averages of the results for high and low values for each of the operating paratemers are contained in Table 4. By comparing the average values in Table 4, an assassment can be made as to which operating parameters have been yhr greatest impact on the TCLP leachability of the final waste form.

It is apparent that waste loading was the most critical operating parameter impacting the product leachability. In every case, the leach results increased as the waste loading increased. Although the magnitude of the impact for this operating parameter was greater than for any other. This result is not surprising since greater waste loading results in higher metal concentration in the final waste form and greater metal availability for dissolution. However, high waste loading is a very desirable characteristic for the final waste form due to its favorable impact on process economics. Obviously, this operating parameter must be fullyo ptimized.

A slight response was observed for frit composition. Higher borax concentration in the frit compositionleachability of the final waste form. resulted in higher TCLP leachability. Borax is a constituent in the glass forming frit added to the sludge before microwave processing. It modifies the melt during the process, thereby lowering the melting temperature of the waste mixture. This is an important operating consideration. Since the process is being conducted in-drum (ie., the waste container), high temperatures could result in failure of the drum. However, as these results show, increasing the borax concentration to lower the melting temperature can lead to undesirable leachability characteristics in the final waste form. Again, this operating parameter must be fully optimized for microwave processing.

Temperature and quench rate did not appear to impact significantly the TCLP leachability of the final waste form. Therefore, it is not critical to optimize these operating parameters.

CONCLUSIONS

These analyses provide an indication of the critical operating parameters for the microwave solidification process; those being waste loading and borax concentration in the glass forming frit. Further work is required to optimize these critical parameter.

These results are very encouraging and support the view that the microwave solidified waste form is highly desirable for the hydroxide precipitation sludge. In fact, it is anticipated that a much broader variability in waste feed composition can be processed than was originally anticipated due to the performance observed in these tests.

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MOLTEN SALT DESTRUCTION PROCESS FOR MIXED WASTES

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ABSTRACT. We are developing an advanced two-stage process for the treatment of mixed wastes, which contain both hazardous and radioactive components (1). The wastes, together with an oxidant gas, such as air, are injected into a bed of molten salt comprising a mixture of sodium-, potassium-, and lithium-carbonates, with a melting point of about 580°C. The organic constituents of the mixed waste are destroyed through the combined effect of pyrolysis and oxidation. Heteroatoms, such as chlorine, in the mixed waste form stable salts, such as sodium chloride, and are retained in the melt. The radioactive actinides in the mixed waste are also retained in the melt because of the combined action of wetting and partial dissolution. The original process, developed by Rockwell International, consists of a one-stage unit, operated at 900–1000°C. The advanced two-stage process has two stages, one for pyrolysis and one for oxidation. The pyrolysis stage is designed to operate at 700°C. The oxidation stage can be operated at a higher temperature, if necessary.

INTRODUCTION

Mixed wastes are hazardous wastes that are also radioactive. Acceptable methods for the treatment of mixed wastes are not currently available. The Molten Salt Destruction Process (MSD) is an alternative to, and offers several advantages over, incineration. MSD was originally developed by Rockwell International as a single stage process for coal gasification, and later used for treatment of hazardous wastes, such as polychlorinated biphenyls (PCBs) (2). MSD differs from incineration in several ways: there is no open flame in MSD, the containment of actinides is accomplished by chemical means (wetting and dissolution), the operating temperature of MSD is much lower, thus lowering the volatilities of radioactive actinides, and no acid gases are generated in MSD. These differences provide the main reason for developing MSD as an alternative to incineration.

In MSD, mixed wastes are introduced into a bed of molten salt (typically alkali metal carbonate), together with air or oxygen (Fig. 1). The organic components of the mixed waste are converted into CO_2 and H_2O, heteroatoms such as chlorine form stable salts such as sodium chloride, and the actinides are retained in the melt through dissolution and wetting. The lower operating temperature of the process (700–900°C, compared to 1000–1200°C for incineration) keeps the actinide volatilities lower than what would be expected at higher temperatures. At the termination of a run, the salt can be drained out, and dissolved in water. The oxides and salts of actinides, being insoluble in the alkaline solution, precipitate and are filtered out. The dissolved salts are separated by crystallization. The carbonates are recycled back to the reactor, and the stable salts are disposed of as low level waste (LLW). The products of the MSD process are either benign gases (CO_2,H_2O), concentrated actinide oxides/salts, or low level waste, thus resulting in a large volume reduction from the original mixed waste. Treatable waste streams consist of organic liquids (including the ones containing chlorinated solvents and PCBs), greases, and combustible solids such as cellulosic matter, rubber and plastics.

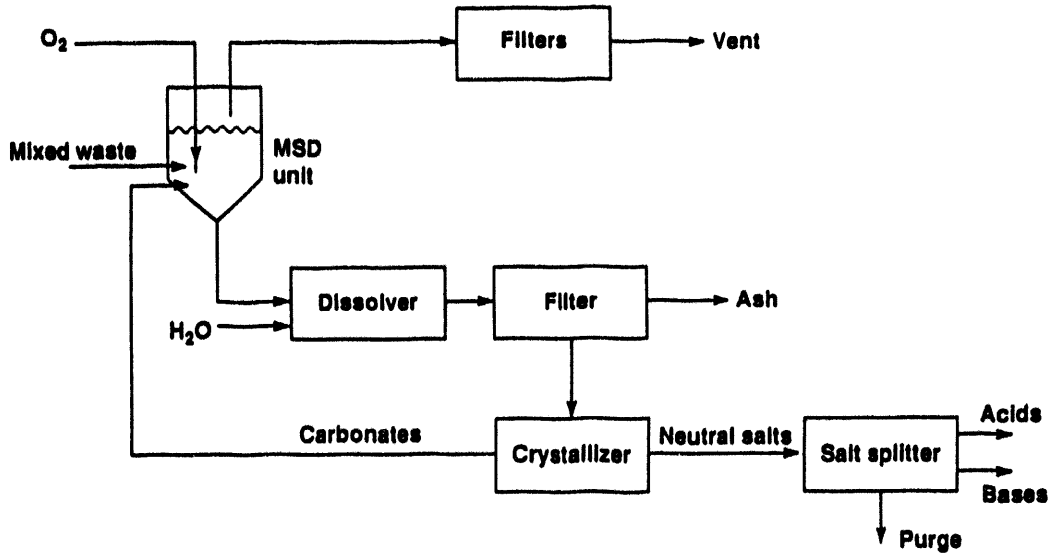

Figure 1. Mixed waste flow sheet using molten salt.

TECHNICAL BASIS

The molten salts are typically mixtures of alkali or alkaline earth carbonates and halides. The salts provide excellent heat transfer and reaction medium, catalyze oxidation of organics, and prevent formation of acidic gases (e.g., HCl, SO_2, and P_2O_5) by forming instead solutions of their neutral (and stable) salts (e.g., NaCl, Na_2SO_4, and Na_3PO_4) (2,3). The relatively high thermal inertia of the melt tends to resist changes in temperature resulting from sudden changes in the feed or heat transfer. The melt avoids the formation of potentially fugitive radioactive particulates and molecular species by a combination of particle wetting, encapsulation and dissolution with complex formation. Therefore, containment of the radioactive material is based on a physico-chemical process rather than on mechanical means alone, as is the case with incineration.

The melt must remain fluid for contacting of the waste with oxygen, wetting the particulates, and transfer of the melt. For wastes containing substantial quantities of inorganic oxides, (e.g., paper products containing kaolin), the "ash" builds up as either dissolved substances or to form a slurry, resulting in increase of viscosity and loss of fluidity. In this case, a fraction of the melt can to be removed, and replaced by fresh salt. The withdrawn melt can be processed as shown in Fig. 1. If the salt accumulates high concentrations (20–30%) of alumina and silica while the process is operated under oxidizing conditions, the alumina and silica combine to form solid deposits on the vessel walls (1). This phenomenon is not observed during oxygen deficient conditions (i.e., in the pyrolysis mode), or in the presence of silica or alumina alone. This observation has led us to develop the advanced two-stage process wherein the first stage is operated under reducing conditions, and the second under oxidizing conditions. In this mode of operation, the main reaction undergone by the organic portion of the waste is pyrolysis, with partial oxidation of the pyrolysis products. The acid gases are, however, completely avoided by formation of their respective salts, and the acinides, along with the ash, are retained in the melt. The ash may now build up to higher levels than those that limit operation under oxidizing conditions, with no chance of a melt freeze-up. The products of pyrolysis from the first stage are completely oxidized in the second stage, which is operated with excess oxygen. The second stage also acts as a "polishing" step for cleaning up residual amounts of acid gases, and for retaining any entrained actinide particles; it operates without ash build-up under near optimal process conditions.

EXPERIMENTAL PROGRAM

We have built a two-stage experimental unit to investigate the applicability of the molten salt destruction process to the treatment of mixed wastes. Figure 2 shows a schematic of the current configuration, while Fig. 3 shows an isometric sketch of the unit.

The two crucibles, physically identical, are made of stainless steel. (Stainless steel is stable in the presence of alkali carbonates, but susceptible to stress corrosion in the presence of chlorides. The crucibles can be subjected to a maximum of 47 thermal cycles based on a safety analysis of the welds. This limit is considerably lower than that imposed by chloride corrosion.) They have the dimensions 5.76" ID, 6.63" OD, and 37.75" length. They are fitted with a drain pipe at the bottom and a flange on the top. The drain pipe leads to a drain bucket, large enough to contain the molten salt inventory, which is placed under each crucible. The waste to be treated and the oxidant gases are introduced through a feed tube near the center of the crucibles. The gaseous product of the first crucible is sent to the second crucible for complete oxidation. The oxidant gas for the second crucible is introduced separately into the second feed tube. The off-gas from the second crucible passes through a cold trap, cooled by a central water tube, to capture entrained liquid droplets. Three cylindrical electrical heaters, each rated at 3 kW, are placed outside each crucible. A smaller fourth heater is located under each crucible, concentric with the drain pipe. A blower is placed under the crucibles to blow air through the annular space between the crucibles and the heaters. The heaters are needed for starting up the process, whereas the blower is needed to remove the heat generated by oxidation of wastes. The off-gas from the cold trap is passed through a Bickley furnace to ensure complete oxidation of any trace contaminants, and then through high efficiency particulate air (HEPA) filters before being vented.

A number of thermocouples are placed at various locations, both inside and outside the crucibles, to keep track of temperatures. The pressures within the crucibles, and the differential pressures around the filters are continuously monitored, as are the feed rates of the waste and the oxidant gases. A residual gas analyzer is used to monitor the gas compositions. Gas samples can be taken through a number of sampling ports for a more accurate off-line analysis. We use a data logger/controller program to continuously save the data and to control the operation of the unit.

We have completed construction of the unit as described above. The shakedown runs have been completed. The unit is currently operating on waste simulants, such as dodecane and ethylene glycol.

In addition to the main program, we have several smaller supporting programs underway. We have built a plexiglass model of the crucible, which is dimensionally identical to the stainless steel crucibles, to conduct fluid flow experiments. This allows us to measure the variation of the froth height with respect to the gas flow rate, liquid height, liquid surface tension and viscosity, and inlet nozzle configuration. We have developed sensors to monitor the froth height on-line. Another experimental system is being used to study the effect of melt composition and ash loading on the melt viscosity. Finally, we have a number of corrosion studies underway to study the effect of the melt composition on different crucible materials.

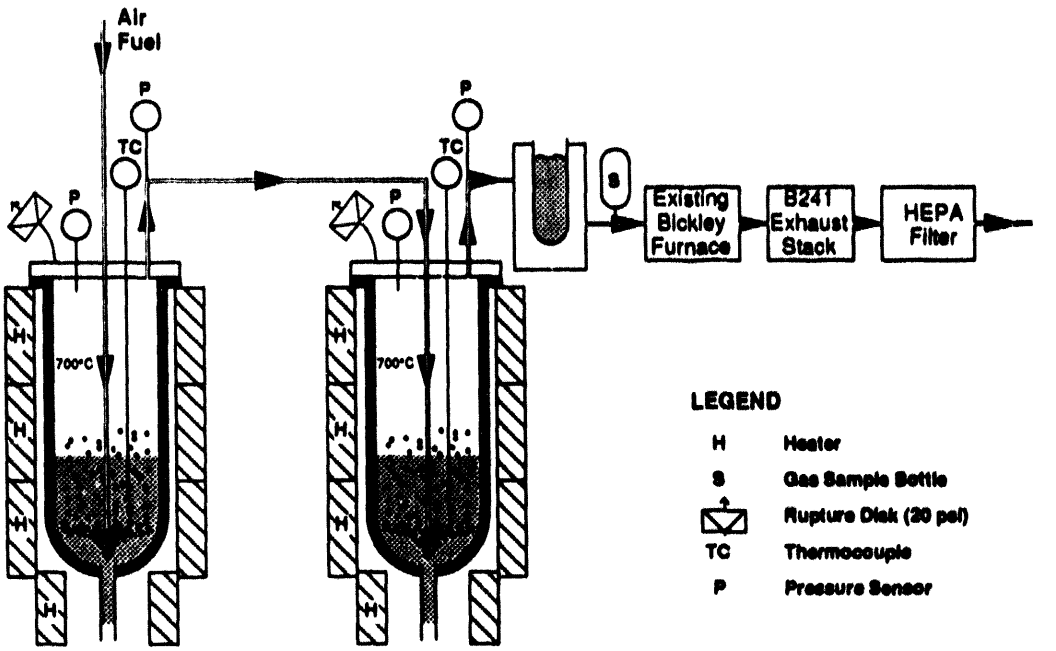

Figure 2. Schematic of the two-stage experimental unit.

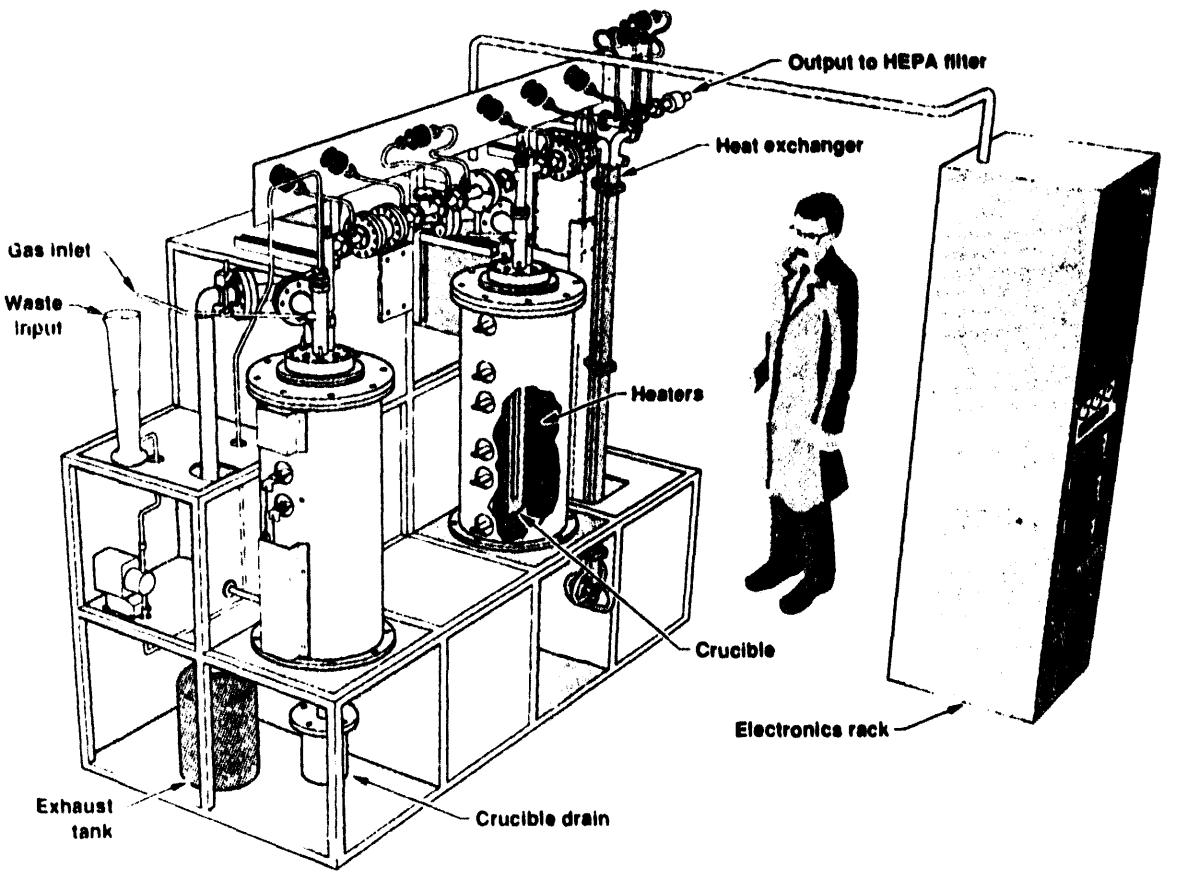

Figure 3. Isometric sketch of the two-stage experimental unit.

RESULTS AND DISCUSSION

We have developed correlations for gas hold-up as a function of gas velocity, liquid height, and nozzle height based on our experiments on air-water and air-oil systems in the plexiglass model. These correlations have been extended to liquids with surface tensions significantly different from that of water. These correlations allow us to predict the froth height in the actual system for any configuration. In addition, our studies using color tracers have demonstrated a thorough mixing of the contents of the liquid phase for gas flow rates significantly less than those anticipated in real operation.

Krikorian has performed thermodynamic studies on the volatilities of radionuclides and toxic elements in the molten salt destruction process (4), and on the selection of salt mixtures (5). His analyses show significantly lower (orders of magnitude) volatilities for actinides at the molten salt temperatures compared to the temperatures of typical incinerators.

CONCLUSIONS AND FUTURE WORK

The process analyses conducted by Rockwell International (6) demonstrate that the molten salt destruction process is a viable option for the treatment of mixed wastes. A number of critical uncertainties, however, must be resolved:

- The effect of ash on melt stability under a variety of operating conditions.
- Processing of the spent salt under the limiting conditions of the build-up of ash and stable salts (such as sodium chloride).
- Retention of particulates in the molten salt bed.
- Tolerance to upsets under a variety of operating conditions.

The experimental program currently underway is designed to address these issues and to obtain sufficient process engineering data to design a pilot-scale unit. A more detailed description of the planned facility to house the pilot scale experiments is being presented at this conference by Brummond and Celeste from the Lawrence Livermore National Laboratory.

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MOLTEN SALT OXIDATION OF RADIOACTIVE HYDRAULIC OIL WASTE

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ABSTRACT. Molten Salt Oxidation (MSO) technology, developed by Rockwell International from the 1970's through the early 1980's, yielded results which indicated an excellent potential for treating hazardous and radioactive wastes; however, interest in MSO declined in the late 1980's because of the availability of less expensive treatment technologies. The U.S. Department of Energy has recently shown interest in MSO because of its potential advantages over existing processes in the treatment of mixed wastes.

MSO can be characterized as a simple-non combustion process; the basic concept is to introduce air and wastes into a bed of molten salt (usually sodium carbonate at 900-1000 C), oxidize the organic wastes in the molten salt, then use the heat of oxidation to keep the salt molten. It also retains many undesirable oxidation products, such as acidic gases and metal vapors and thus requires no wet scrubbing system for off-gas treatment; the salt with its adsorbed reaction products is removed for disposal or processing to remove the undesirable waste with recycle of the salt for reuse. The MSO process has been developed through pilotscale testing, with successful destruction of a wide variety of wastes.

This paper reviews the principles and capabilities of MSO and briefly describes results of a program in progress to demonstrate MSO for the treatment of mixed wastes. Results of a campaign in which 50 gallons of radioactive hydraulic waste oil was destroyed is highlighted.

INTRODUCTION

The Molten Salt Oxidation (MSO) process has been developed by Rockwell International over a span of 30 years. Starting in the 1950s, Rockwell International conducted theoretical and experimental studies on molten salts. These initial studies focused mainly on the chemical and physical properties of molten salts, including evaluations of their thermodynamic and transport properties, the interaction of molten salts with molten metals and the behavior of molten salts at high pressure.

Rockwell International's understanding of the versatility of molten salts evolved during the course of this initial work; later studies examined the use of molten salts to scrub sulfur oxides from flue gases and as a catalyst for gasifying coal (1). During the coal gasification tests, other applications of MSO became apparent, including volume reduction of radioactive waste, destruction of hazardous waste, propellants and explosives, and for metal recovery.

In the 1970s and early 1980s, MSO was developed through bench-scale and pilot-scale test programs in which the process was applied to treatment of radioactive and hazardous wastes including chemical warfare agents, combustible solids, halogenated solvents, polychlorinated biphenyls, plutonium-contaminated solids and uranium-contaminated solvents (2-18). Outstanding features of the MSO Process, which makes it an attractive candidate for processing of mixed wastes, is the 99.9999% destruction efficiency of hazardous

organic constituents along with excellent salt retention of radioactive species, such as actinides and rare earth fission products. The retained elements can be recovered from the spent salt using conventional chemical processes, such as ion exchange, to render the salt nonradioactive and nonhazardous.

At the time of its development, MSO was marginally economically competitive with conventional incineration techniques and thus was not commercially deployed. However, the U.S. Department of Energy has recently shown interest in MSO because of its potential advantages over existing processes in treating mixed wastes (hazardous and radioactive). Initial results of a new program to demonstrate D.O.E. the process for the treatment of mixed wastes are presented in this paper along with a review of the principles of operation and capabilities of the MSO Process.

DESCRIPTION OF MSO

MSO can be characterized as a simple-noncombustion process. Its basic concept (Fig 1) is to introduce air and wastes into a ceramic-lined vessel containing a turbulent bed of molten salt, oxidize the organic wastes in the molten salt, then use the heat of oxidation to keep the salt molten. The salt is removed for disposal or for processing and recycling. The features that distinguish MSO from other oxidation technologies are the catalytic action of selected salts for the oxidation of organics, high heat transfer coefficients, retention of metals and ash in the molten salt, and neutralization and absorption of acid gases in the salt.

In the process, air and waste are continuously introduced beneath the surface of the molten salt which is near atmospheric pressure. Selected air velocities give appropriate molten saltair-waste contact times in the expanded and turbulent molten salt bed. This contact time at temperatures of 9000° C promotes a high destruction efficiency of the organic waste; air in excess of stoichiometry for oxidation of the waste also favors this. An engineering compromise is made between factors such as destruction efficiency, melt contact time, heat transfer, and melt entrapment loss.

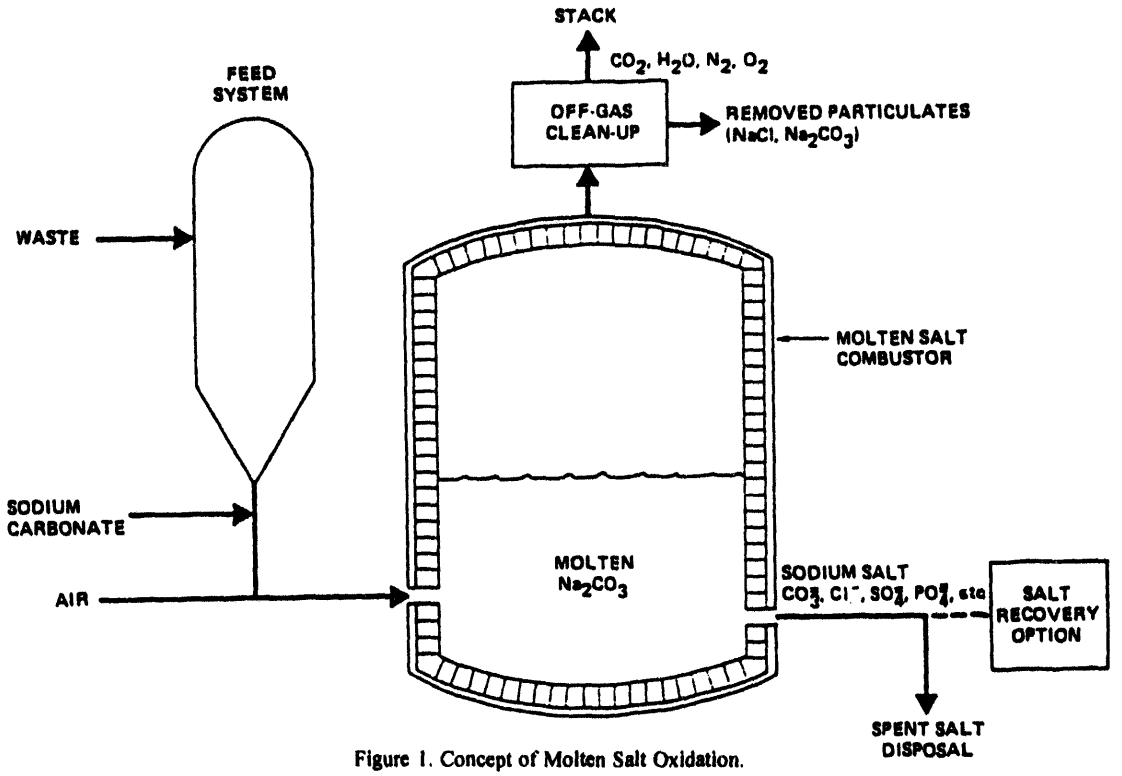

Figure 1. Concept of Molten Salt Oxidation.

The feed stocks may be solids, slurries, organic liquids, aqueous solutions, or gases. In current designs, materials are transported into the bed by pneumatic conveying. While most waste materials that are appropriate for treatment by MSO will have sufficient heat of oxidation to keep the salt molten, some wastes with low heating values may require supplemental heat from fuels such as natural gas, kerosene, or fuel oil. The combustible material is added in such a manner that any gas formed during oxidation is forced to pass through the melt before it is emitted into the atmosphere.

The salt temperature is uniform throughout the well-mixed liquid pool; thermal inertia of the molten salt prevents rapid temperature changes, which makes temperature control of the reaction excellent. Sodium carbonate, or sodium carbonate mixed with other salts (e.g., sodium sulfate, sodium chloride, or potassium carbonate), is typical of the salts used as the melt. During system start-up, it is necessary to preheat and load the salt bath. The operating temperature may range from 700 to 1200 C. At these temperatures, the molten salt has a viscosity similar to water. Temperature control of the salt bed is maintained by a combination of means; these include addition of auxiliary fuel to waste feeds, cooling of the outside surface of the oxidizer vessel with forced air, salt recycle, and adjustment of the oxidizing air feed rates. The primary means are auxiliary fuel addition for wastes with low heating values and forced air cooling for wastes with high heating values.

The off-gases, carbon dioxide, steam, nitrogen, and un reacted oxygen must be cooled and filtered to remove particulate matter. A fabric baghouse-style filter followed by a high-efficiency particulate air (HEPA) filter is the most commonly used off-gas cleanup system for radioactive wastes. Acid scrubber units are unnecessary because all the acid gases, such as HCl, HF, SO_2, and P_2O_5, are instantly neutralized and absorbed by the alkali carbonate molten salt. The resulting neutralized salt is retained in the melt along with residual ash and inert materials.

The molten salt is typically recycled when the dissolved impurities content is high enough to have a negative effect on acid-gas retention or other operating parameters. Undissolved impurities include various metal oxides and silicates. Dissolved impurities are primarily salts such as sodium chloride, sulfate, or phosphate. The concentration of the halide salt or ash that is in the sparged salt bed is controlled by either continuously injecting makeup salt and overflowing the bed or by fill/drain batch operation of the oxidation vessel. The method of salt removal (batch or continuous) is dependent primarily on the composition and rate of the waste feed.

There are several options for the ultimate disposal of the spent salt. If the spent salt is non-hazardous, it might be disposed in a land fill. When radioactive-containing wastes or hazardous wastes are destroyed, disposal of the salt will depend on the regulations of the specific disposal site. In cases of low-level radioactive contamination, the salt is an acceptable waste form. In cases of high levels of residual radioactivity, the waste salt residues may have to be immobilized by chemically or physically transforming them into a non-leachable form before approval can be obtained to dispose of the wastes. It is possible that the salt can be immobilized by glassification or by incorporation into a concrete matrix to form a non-leachable product. The latter option is favored for low waste throughput, where volume reduction of the waste salt is a secondary consideration. The quantity of contaminated waste can be further reduced by aqueous processing; the recycle operation must be designed for the specific impurities involved. Recycling typically consists of dissolution of the salt in water, filtration to remove insoluble, and fractional crystallization of the filtrate to separate dissolved salts. These are commonly used technologies that are adapted for use with the MSO process. The aqueous filtrate is internally recycled so no aqueous secondary wastes are produced.

DESCRIPTION OF MSO EQUIPMENT

A schematic of the bench-scale molten salt reactor is shown in Fig 2. The molten salt is contained in an

alumina tube placed in a stainless steel retainer vessel. The retainer vessel is contained in a furnace. Temperatures are controlled by an SCR controller. The entire system is in a walk-in hood.

The liquid waste feedstock is contained in a stainless steel beaker. Continuous mixing of the liquid is provided by a magnetic stirrer. A peristaltic pump forces the liquid waste into the center tube of the injector. Air is fed into a surrounding concentric tube. This arrangement serves to mix the liquid waste with air; this waste-air mixture passes downward through the injector and emerges into an alumina feed tube. The waste-air mixture is forced to pass downward through the feed tube, then exits into the ceramic vessel containing the molten salt, and then upward through the expanded salt bed. The off-gas from the MSO vessel is cooled, passed through pre-HEPA and HEPA series filters to remove particulate, then discharged to the hood exhaust vent. A portion of the exhaust gas from the HEPA filter is continuously removed, dried, then passed through an additional HEPA filter, before being analyzed for NO_x, CO, $C0_2$, 0_2, and unburned hydrocarbons.

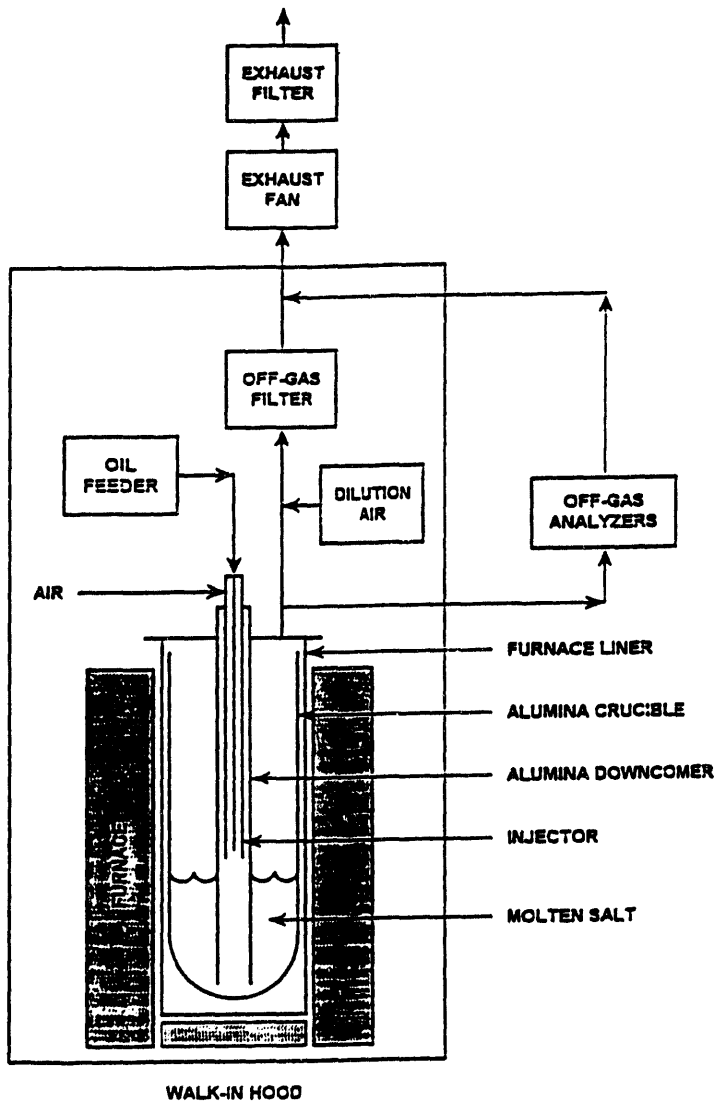

Figure 2. Simplified Diagram of the Molten Salt Oxidation Unit.

Between experiments, the molten salt is maintained at the desired temperature with the electric furnace. When waste destruction is initiated, the heat input to the furnace is generally turned off, since heat generated by oxidation of the organic material is usually sufficient to maintain the molten salt bed at the desired operating temperature. However, with low heating value wastes, especially with aqueous solutions, it may be necessary to inject auxiliary fuel to supply additional heat.

The pilot-scale MSO system consists of a vertical steel tank approximately 22 ft high with a 4 ft outside diameter. It is internally lined with a 6 in.-thick refractory liner made from high-purity, fused-cast alumina blocks. Four injection nozzles are provided on the vessel, located 900 apart from each other. Two of the opposing nozzles are used for injection of air. The other two opposing nozzles are used for solids/fuel/waste/salt injection. One of these two nozzles also serves as a drain through which salt is tapped to empty the unit at system shutdown. Off-gases from the vessel are routed through a short refractory-lined discharge line, the drop-out box and to the baghouse prior to being discharged to the atmosphere.

NEW DOE MSO PROGRAM

A DOE-sponsored three-day peer review of the Rockwell-ETEC MSO process was held in November 1991 to establish its present and potential readiness for application of MSO to the treatment of mixed waste. The peer review panel judged that the process was applicable to a variety of mixed waste types; rapid implementation of the technology was recommended (17). The panel also concluded that MSO was ready to be applied to the wastes of Hanford and Oak Ridge, as well as to the wastes of other sites such as, INEL, Savannah River, Rocky Flats, Rockwell-ETEC and DOE national laboratories.

At the Peer review, the mixed wastes were classified into four categories, based on the state of readiness of the process for different wastes. Category 1 consisted of wastes for which the process can be developed for near-term application. These included organic liquids, including chlorinated wastes, and contaminated gases. The contaminated gases could be the off-gas from a first-stage thermal treatment, such as incineration. The extremely good destruction efficiency of MSO lowers the probablistic risk of hazardous waste discharge to the environment from an incinerator or similar thermal process. Category 2 consisted of wastes for which the process is applicable but more extensive development work is required. These consisted, for example, of combustible solid wastes which pose potential feeding problems. Category 3 consisted of wastes such as hazardous salts, where some safety aspects must be resolved by longer term studies and although some tests with such wastes have been conducted successfully on a bench-scale system. Category 4 consisted of wastes which were not recommended for the molten salt process. These include such wastes as soils, metal parts and wastes containing a substantial amount of metal parts, rubble or ash.

RESULTS TO DATE

Approximately 50 gallons of highly diverse waste oils, ranging from light hydraulic oil to heavy, sludge-laden 140 weight gear oil as well as multiphase mixtures of organic degreasers, solvents and alcohols were destroyed by MSO at ETEC. The wastes were slightly contaminated with radionuclides such as ^{137}Cs and ^{60}Co. This bench-scale demonstration run was part of a larger DOE five-year implementation program for disposal of mixed wastes. The purpose of the 1992 MSO program, of which this bench-scale demonstration was the central effort, was to achieve two primary goals. These included a third-party confirmation of high destruction efficiency (DE) and to show a capability to destroy a diverse set of actual mixed wastes. The processing run produced new data for long-term operation of a molten salt system.

In the 1992 test program, sodium carbonate (Na_2CO_3), maintained at 900^0 C, was used as the molten salt reaction bed. The mixed waste was injected into the salt bed with excess oxygen. The superficial gas

velocity through the molten salt bed was maintained to produce a well-mixed system. HEPA-type filters in the effluent gas stream were used to remove the salt particles from the off-gas. The off-gas was continuously monitored for $C0_2$, CO, hydrocarbons and NO_x content by on-line electronic instrumentation. No aqueous off-gas scrubbing system was needed.

The program was conducted following an around-the-clock time schedule. Health Physics support was provided with continuous radioactive surveys of the work environment areas as well as radioactive (RA) analysis of the input feedstock and salt samples. Long-term MSO operation with radioactive wastes was thus demonstrated. The EPA sampling methods employed, along with up-to-date instrument monitoring of the effluent gases, conservatively demonstrated that the destruction efficiency of the chemical wastes exceeded regulatory requirements. The RA content of the melt and of the particulate from the HEPA exhaust line filters were measured and compared to the RA input from the waste oil feedstock. Evaluation of the test results indicated that the chemistry of the melt can significantly affect the percentage of radionuclides and metals retained within the melt. A preliminary analysis of the retention of ^{137}Cs and ^{60}Co during the oil processing was calculated on the basis of the prefilter and oil feed analyses. The melt retention during a period with sodium carbonate-sodium sulfate melt was 85% for ^{137}Cs and 99% for ^{60}Co. The melt retention during a carbonate-only period was 53% for ^{137}Cs and 72% for ^{60}Co. The retention for both elements was significantly improved by the presence of sulfate in the melt. Supporting research to improve the retention beyond 85-99% has begun.

CONCLUSIONS

Molten salt oxidation is an emerging technology which is attractive for treatment of mixed hazardous and radioactive waste. The use of a molten salt medium provides several advantages over combustion techniques such as incineration. The molten salt: 1) acts as a dispersing medium for both the waste being processed and the air used in the processing; 2) provides a catalyst for the oxidation reactions and accelerates the destruction of organic material; 3) enhances completeness of the chemical reactions by providing better contact over a relatively long time period and provides a stable heat transfer medium that resists thermal surges; 4) neutralizes and retains acid gases; 5) helps retain soot and chars in the melt for more complete reaction; and 6)retains the ash, metals, and other noncombustible material associated with the waste. MSO is particularly well-suited for combustible waste streams such as organic liquids and combustible solids. The catalytic action of the salt produces extremely good destruction at operating temperatures less than typical incineration processes; the chemical affinity as well as the dilution effect of the salt inhibits the release of metals into the off-gas. Further evaluation of process economics, public and regulatory acceptance, large-scale operation, materials lifetime, and other engineering issues are being addressed to implement the process at DOE facilities.

This 1992 MSO test program demonstrated the inherent capability of the MSO process to successfully dispose of a diverse set of actual mixed wastes at destruction efficiencies of 99.9999%. The MSO destruction campaign was especially valuable in providing leads to areas of research and development which have the potential to significantly improve the mechanical and chemical performance of MSO technology.

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THE PLASMA HEARTH PROCESS TECHNOLOGY DEVELOPMENT PROJECT

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ABSTRACT. The U.S. Department of Energy (DOE) Office of Technology Development (OTD) is currently evaluating the Plasma Hearth Process (PHP) for potential treatment of several DOE waste types. The PHP is a high-temperature vitrification process that has potential application for a wide range of mixed waste types in both the low-level and transuranic mixed waste categories. The PHP is being tested under both the OTD Mixed Waste Integrated Program and the Buried Waste Integrated Demonstration. Initial testing has been completed on several different surrogate waste forms that are representative of some of the DOE mixed waste streams. Destruction of organic material exceeds that of conventional incineration technologies. The vitrified residual has leaching characteristics comparable to glass formulations produced in the high-level waste program. The first phase of the PHP demonstration project has been successfully completed, and the project is currently beginning a comprehensive second phase of development and testing.

INTRODUCTION

The U.S. Department of Energy (DOE) Office of Technology Development is responsible for the development of new treatment technologies that can fulfill the requirements for the unique waste problems facing DOE. Treatment technologies are needed for a wide range of waste classification types including: transuranic waste (TRU), mixed TRU, reclassified TRU, low-level waste and low-level mixed waste. These wastes represent a wide range of physical properties and chemical compositions. There is currently no widely accepted, proven technology commercially available that is applicable to a majority of these wastes, especially for TRU or other alpha-contaminated wastes. Many technologies rely on extensive segregation and pretreatment of waste materials in order to effect treatment, which increases handling, radiological exposure potential, and cost. Often, multiple technologies have to be used for treatment of the entire waste stream. Therefore, DOE is developing treatment technologies that can accept and process a wide range of materials without need for pretreatment, especially dissimilar materials combined in a single matrix.

A significant portion of the DOE radioactive wastes are contaminated with hazardous organic and/or heavy metal constituents (referred to as mixed wastes), and will therefore be subjected to U.S. Environmental Protection Agency (EPA) requirements. In particular, mixed waste will have to be disposed of in accordance with the EPA's Land Disposal Restrictions (LDRs). The LDRs require treatment of hazardous wastes to defined standards before permanent disposal is allowed. Treatment technologies for mixed waste will have to provide treatment to current LDR standards. Wastes requiring both destruction of organics and stabilization of heavy metals (as well as radionuclides) will present a particularly complex waste treatment need, often requiring a multi-step processing concept.

Characterization of mixed waste, particularly alpha-contaminated waste, will be difficult and expensive to accomplish. At this time, DOE is relying heavily upon process knowledge to provide the characterization information needed; however, much of the waste now in storage has been generated as long as twenty years ago, which has caused regulators to question this method of characterization on occasion. Characterization

for disposal requires a very rigorous assessment of the contents of the waste. Many conventional treatment technologies require a thorough characterization to identify and screen out materials that are not compatible with the process. Characterization generally means a high degree of handling and thus potential exposures, as well as increased cost. Technologies that will minimize characterization requirements, both before and after processing, will be advantageous.

The Plasma Hearth Process Treatment Concept

DOE is conducting a project to evaluate the Plasma Hearth Process (PHP), a high-temperature, fixed-hearth arc plasma technology that has been used for many years in the processing of specialty and other metals. The type of plasma being considered in this application is referred to as a thermal plasma, and uses a "torch" to generate the plasma. The PHP concept, when applied to waste treatment, produces a very stable, vitrified final waste form that will be in full conformance with LDR standards.

Because of the high operating temperature, the PHP can be a very robust process, should be relatively insensitive to waste feed variations, and is therefore potentially applicable for treatment of a wide range of DOE waste types. Being a robust process, there is little to no need for segregation or pretreatment of waste materials prior to feeding. In fact, the hearth design allows processing of bulk quantities of waste material contained in whole drums directly to a final waste form in a single processing step. Similarly, characterization requirements will be reduced, again because of the versatility of the process.

THE PHP DEMONSTRATION PROJECT

The PHP development project will be accomplished in three phases. The first phase has recently been completed, and its results are described in this paper. As a proof-of-principle demonstration, the Phase 1 tests evaluated the feasibility of PHP treatment of a range of expected DOE waste types, and demonstrated some of the more important characteristics of the PHP, including the following: the ability to process a wide range of materials; the ability to accept whole drums full of waste as a feed; the efficacy of destruction of organic material; and the production of a stable, leach resistant vitrified final product.

Phase 1 Test Equipment Description

A laboratory demonstration PHP system was designed and fabricated for the Phase 1 testing. A schematic of the PHP test apparatus is shown in Fig. 1. The system was designed by Science Application International Corporations (SAIC) and was constructed and operated by Retech, Inc. at their test facility in Ukiah, CA. The demonstration-scale system is designed to be at or near what is anticipated to be full-scale (nominally 1 MW), and is capable of accepting full-size unopened drums filled with surrogate waste materials. For purposes of Phase 1 testing, the system design was kept very simple. Phase 2 of the project will provide for the design and testing of a more operationally complete prototype system.

The main component of the system is the primary reaction chamber, where the plasma torch is installed. The chamber is a refractory-lined, water-jacketed steel vessel with an internal volume of approximately 100 cubic feet. The system uses a DC transferred arc plasma torch to provide the process heat in the primary chamber. The torch is primarily operated using nitrogen as the plasma gas, but can also be operated on air. Drums are fed into the primary chamber using a pre-loaded ram feeder mounted on the side of the primary process vessel.

The waste drums are slowly fed into the chamber and "dripmelted" into a water-cooled, refractory-lined crucible. The organic fraction of the waste will volatilize, pyrolyze, and partially combust. The remaining inert materials (bulk metals, silica, alumina, etc.) form a molten pool in the crucible. For purposes of the Phase 1 demonstration, this system was designed such that upon complete melting of the inert materials,

the system is shut down and allowed to cool. After cooling, the mold is removed and the solidified inert products are sampled for analysis. A future prototype system will be designed such that molten materials will be removed on a continuous basis.

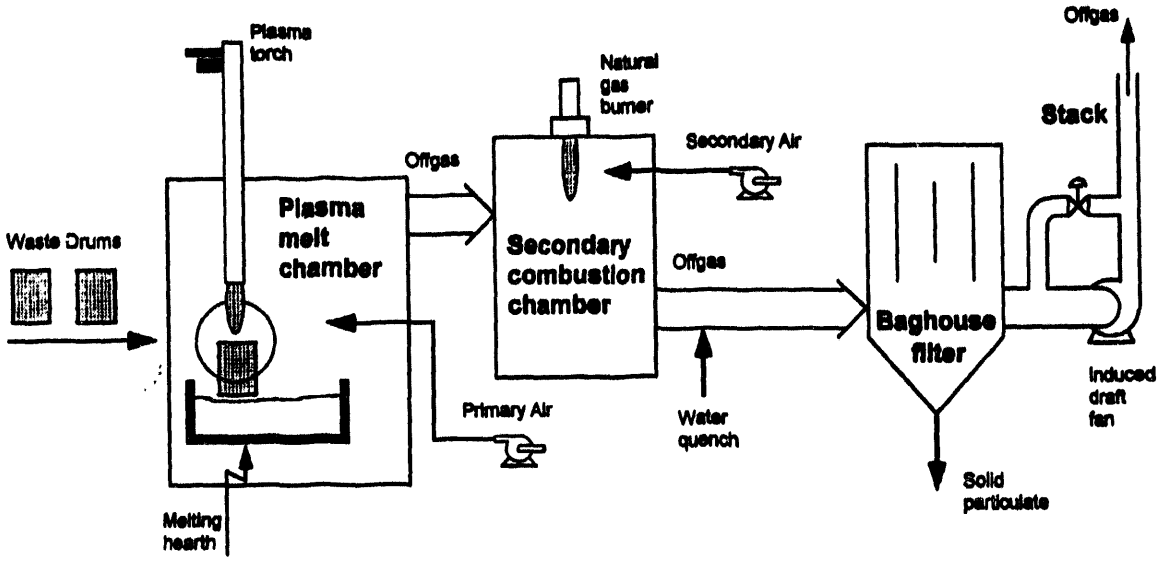

Fig. 1. Schematic of the PHP Test Apparatus

The volatilization and combustion products of the primary reaction are drawn from the primary chamber as offgas and introduced into an afterburner to complete the combustion reaction. The afterburner is a cyclonic secondary chamber designed for a 2 sec residence time at 1800 °F (982°C). Excess air is introduced into the chamber and contacted with the process offgas to accomplish the combustion. A natural gas burner is used to provide a source of heat in the secondary chamber when needed. The temperature is always maintained above 1400 °F (760°C) to assure ignition of the offgas.

The process offgas from the secondary chamber is drawn off and passed through an offgas treatment system. For purposes of this demonstration, only simple feed materials were used, and offgas system design was thereby simplified. First, the offgas is quenched by an air atomized water spray to remove process heat, reducing the temperature to below 450 °F (230°C). Any particulate entrained in the offgas is then filtered out through the use of a high temperature pulse-jet baghouse. An induced draft fan, located on the exit of the baghouse, promotes the flow of offgas in the system and maintains the primary chamber at a slightly negative pressure.

Testing Conducted

Two distinct series of tests were conducted in this first phase of testing (2). The initial waste form tested was a simulated Rocky Flats Plant (RFP) TRU supercompacted waste form. The primary reason for testing this waste form was because the dense nature of the waste makes it extremely difficult to treat by conventional treatment processes. The testing was conducted on non-hazardous, non-radioactive surrogate waste material that was placed into 35-gal steel drums and "supercompacted" in a 500-t hydraulic press. The whole compacted drums were fed to the PHP for processing without any pretreatment.

A review of existing data from past RFP TRU waste characterization efforts revealed that the majority of waste that will be supercompacted at RFP falls into two categories: combustible waste and bulk metal waste (3). These two categories comprise over 80% (weight basis) of the waste that will be supercompacted, and

so the Phase 1 tests were structured to demonstrate processing of each of these two waste categories. The combustible waste tested consisted of plastic, paper, rags, wood, etc., and was intended to simulate waste that is routinely generated during normal nuclear operations. The metal waste tested consisted of iron, steel, aluminum, copper, etc., mainly in the form of process component shapes (e.g., valves, pipes).

The second half of the Phases 1 testing was conducted to evaluate the application of the PHP for buried waste applications. The buried waste matrices were selected to represent the major waste types that will need treatment during a planned remediation of the Idaho National Engineering Laboratory Subsurface Disposal Area (4). The simulated buried waste matrices tested include a soil only matrix, a high metal content matrix, a high combustible content matrix, two simulated sludge wastes, and a mixture of all of these together. The metal waste and the combustible waste were similar to the two RFP waste forms tested, but were not supercompacted. One of the sludge waste forms represented a high water content metal oxide sludge, and the other sludge was a high Btu content organic sludge (oil and grease mixed into a stabilizing agent). The testing was conducted feeding full 30-gal drums of simulated waste materials interspersed with soil to simulate the retrieval scenario where waste drums have deteriorated significantly and are retrieved in a manner where the waste materials are mixed with soil and repackaged into drums for handling.

RESULTS OF TESTING

The primary intent of the Phase 1 testing was to demonstrate the ability to process whole, intact drums of a wide range of waste materials in an "as-received" condition, and process those drums directly into a final vitrified residual without pretreatment. The feed materials were selected to be representative of waste that is not pretreated. The waste packages were prepared by loading the materials is a random fashion so that segregation of materials was minimized.

Of the range of materials described previously, all waste types processed very well, with complete conversion of heterogenous materials into a much more homogeneous final product. The progress of the drum processing was monitored using a video camera image of the inside of the primary chamber taken through a pin-hole lens in the side of the chamber. The video image was monitored at the at the main control console. Process parameters (temperatures, flows, offgas composition) were monitored during feeding to look for changes that indicated loss of process control necessitating system shutdown. In general, successful stable feeding was achieved during all test series. No process upsets were noted as a result of feeding the drums into the primary chamber, and no unplanned shutdowns were required due to instability resulting from feed material. Average processing rates ranged from 210 lb/hr for highly combustible feeds to 560 lb/hr of noncombustible feeds.

Environmental Performance

The destruction of organic material was evaluated by the ability of the PHP to destroy bulk organic material and by standard EPA accepted measurements to indicate the likelihood that the PHP will be able to meet EPA criteria for hazardous organic destruction (1). A combustion gas analyzer was used to provide an indication of oxygen, carbon monoxide, nitrogen oxides, and sulfur oxides during all test operations. An independent sampling subcontractor provided continuous emissions monitoring (CEM) for two of the runs to assess the quality of the data being generated by the combustion gas analyzer, and also to provide more complete data than that recorded manually.

During processing of waste containing organic material, CO levels in the offgas typically remained well below 100 ppm and oxygen levels were maintained at greater than 8%. During the test run involving the highest combustible loading tested (~13,000 Btu/lb), the offgas sampling subcontractor reported average CO levels below 50 ppm. The total hydrocarbon levels measured during the CEM runs were consistently below detection. These parameters, standard measures adopted by the EPA for evaluating the efficacy of

destruction, indicate that the process is likely to be able to provide the destruction required for hazardous organics.

Analysis of the carbon content was conducted on the residual solid phase products to determine the level of conversion of the organic from the solid to the gas phase. Carbon levels in the residual slag and baghouse dust were extremely low, displaying excellent conversion of organic materials. The vitrified slag had a residual carbon level ranging from less than 0.5% up to 2.5%. Even at the highest combustible loadings tested, the baghouse dust had less than 2% unburned carbon. Both slag and baghouse dust carbon levels meet or exceed the performance of state-of-the-art incineration systems.

An indication of the particulate generation potential was provided by measuring the mass of particulate collected for a particular test, and comparing that to the feed mass. Consistently, the fly ash collected was on the order of 2% of the mass of feed material processed, irrespective of the feed material type. This low value of dust generation is consistent with the design concept of the PHP system as a low particulate generation device. A more comprehensive study of particulate generation, including volatile metals generation, will be conducted as future follow on efforts to this first phase of testing.

An analysis of Method 17 (5) samples taken from the stack gas was conducted during these tests to determine the stack particulate loadings to provide an indication of whether problems may exist. One sample was taken during a metal material test, and one during a combustible material test. In both cases, stack particulate was well below the current EPA standard for particulate discharge. The corrected particulate loadings for both tests were essentially an order of magnitude below the regulatory limit of 0.08 gr/dscf. Table 1 shows the offgas sampling results obtained.

Table 1. Particulate Emissions Summary

Test ID	Actual Loading gr/dscf	Actual Dry Stack O_2 % (average)	Corrected Loading gr/dscf @ 7% O_2	Mass Emissions kg/h
CWT - 7	0.00049	13.8	0.00096	0.00127
CWT - 8	0.00420	13.7	0.00810	0.01727
Reg. Limit	NA	NA	0.08000	NA

Levels of nitrogen oxides (NO_x) in the offgas stream were variable during the testing. Formation of NO_x is dependant on several process operating conditions and parameters. NO_x concentrations were often maintained below 100 ppm, but on occasion were as high as 3,500 ppm. Based on the results obtained in this phase of testing, it is felt that NO_x can be controlled to a large extent through proper control of operating conditions. This will be a subject of future investigation.

Product Quality of the Treated Residual Slag

Slag samples from all tests were subjected to Toxicity Characteristic Leaching Procedure (TCLP) analysis, primarily to assure that the treated residuals would remain nonhazardous materials. No heavy metals were purposely added to any of the waste matrices being tested in Phase 1; however, relatively high levels of chrome and some traces of lead were found in the vitrified residual. The sources of chromium were likely a combination of the stainless steels in the waste matrix and the refractory material of the crucible. Chromium concentrations were as high as 4% of the slag. Lead, likely from pigments in some of the

materials, was only present in trace quantities, and not in every test run. So even though no heavy metal materials were intentionally added to the waste feeds, the presence of the chromium and lead in the final form allows an indication whether the process will produce a treated residual that will meet TCLP criteria. All samples analyzed were found to be well within applicable regulatory limits. Results of the TCLP tests are shown in Table 2.

Table 2. TCLP Results from Plasma Test Slag Samples

		Run Number				
Analyte	Limit	1	2	3	5	6
Ar	5.0	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	100.0	<0.05	<0.05	<0.05	<0.05	0.13
Cd	1.0	<0.05	<0.05	0.05	<0.05	<0.05
Cr	5.0	0.06	0.13	0.44	<0.05	<0.05
Pb	5.0	<0.05	<0.05	0.10	<0.05	<0.05
Hg	0.2	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004
Se	5.7	<0.01	<0.01	<0.01	<0.01	<0.01
Ag	5.0	<0.05	<0.05	<0.05	<0.05	<0.05

Note: Run 4 data were not obtained because the test was not completed due to equipment malfunction.

In an attempt to gain further insight into the leachability characteristics of the slag, samples were also subjected to the Product Consistency Test (PCT) leaching procedure (6). The PCT is a durability test developed in support of the high level waste vitrification program that is intended to provide some measure of the long term stability of the slag or glass sample tested. It is a 7-day leach test using ASTM Type I water at 90°C, with the sample pulverized to -100 +200 mesh, and provides a measure of the percentage of individual constituents that leach from the glass phase. The test provides a standardized, comparative measure of the durability of the glass matrix subjected to testing, is an accepted standard in the high level waste program, and thus allows comparison of the results with those of other engineered glass waste forms.

PCT tests were conducted for a slag sample from both of the high metal content waste feed and the high combustible content waste feed. Neither of these test runs involved adding any glass forming additives or fluxes to improve the slag properties. The PCT test results were compared with those published by Savannah River Laboratory for one of their engineered high-level waste glass compositions (7). Table 3 shows the comparison of normalized concentrations in the leachate for a 7-day PCT leach of PHP slag and SRL 200 glass (7). The glass produced during the Phase 1 PHP test series demonstrates leach resistance comparable to the optimized SRL 200 glass, and in most cases resulted in higher leach resistance, even without the benefit of glass forming additives.

FUTURE PROJECT INITIATIVES

With the successful completion of Phase 1, the project is now in the beginning stages of Phase 2. Phase 2 will be an aggressive development phase to design and develop a second generation PHP system having the operational features needed for a mixed waste treatment process. The first step in Phase 2 will be to

use the current demonstration system to conduct testing involving waste feeds that are spiked with hazardous components. These tests will provide a better indication of the potential environmental performance of the PHP, and will provide design data that will be used to upgrade the system to enhance the performance.

Table 3. Comparison of Normalized PCT Results Between RFP Plasma Test Glass and Savannah River Glass

Element	Normalized Concentration		
	RFP Test Glass 1&2-A-S-02-A	RFP Test Glass 6-A-S-02-A	Savannah River Glass SRL 200
Aluminum	0.093	0.044	-----
Boron	-----	-----	0.981
Potassium	1.555	0.191	0.709
Lithium	-----	-----	0.978
Sodium	0.037	0.157	1.057
Silicon	0.084	0.068	0.460

Following this series of tests, the second generation PHP system will be designed and constructed. This systems will provide for enhanced engineering features such as continuous feed and product removal systems, automated controls and advanced hearth design. The offgas system will be upgraded to expand its capability to handle a wider range of pollutants, and thus a wider range of waste feeds. An expanded variety of material types will then be tested to investigate the range of applicability of the system and to identify any processing limits or potential problem wastes that may exist. This will provide an assessment of the overall range of applicability of the PHP to convert whole drums of a wide range of waste materials directly to an enhanced final waste form.

Another component of Phase 2 will be to design and construct a bench-scale process that will be used to conduct tests on radioactive materials. Testing will initially be conducted on surrogate waste materials spiked with radioactive tracers to determine the fate of radioactive materials in a known, controlled situation. Radioactive component surrogates will be used in conjunction with the tracers to determine how well these surrogates model performance of the real material. This will determine the degree to which surrogates should be used in the nonradioactive pilot-scale testing to indicate radioactive material performance. Finally, actual waste materials will be tested in a treatability study as a final measure of process performance in a real situation.

The program will conclude in Phase 3 with the construction and demonstration of a prototype field-scale plasma process to confirm that the technology will meet or exceed all treatment requirements for the waste materials being targeted for processing. A specific treatment application and location will be chosen for the prototype PHP system, and the prototype design will be tailored for that application. The application and site are to be determined based mainly on the results of Phase 2 testing. Phase 3 of the project is planned to commence in FY-96.

SUMMARY

The Phase 1 tests for the PHP were successful in demonstrating the potential applicability of the technology to many of the DOE waste compositions being considered for treatment. The PHP accepted whole, intact, full-size waste containers containing a heterogenous mixture of waste components and converted those components to a final product in a single step without need for pretreatment processing. In all cases, a stable, relatively homogeneous treated residual was produced, even when a widely disparate range of test materials was used. Destruction of organic materials was very good, with unconverted carbon being only on the order of 2% and with EPA evaluation criteria indicating that the PHP has a high potential to meet destruction standards. The emissions from the process, at this stage of the development, do not appear to present any challenges that cannot be mitigated with currently available technology. Lastly, the PHP should be able to produce an optimal residual product of high durability and leach resistance, even when little to no additives are used.

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TREATING WATER-REACTIVE WASTES

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ABSTRACT. Some compounds and elements, such as lithium hydride, magnesium, sodium, and calcium react violently with water to generate much heat and produce hydrogen. The hydrogen can ignite or even form an explosive mixture with air. Other metals may react rapidly only if they are finely divided. Some of the waste produced at Los Alamos National Laboratory includes these metals that are contaminated with radioactivity. By far the greatest volume of water-reactive waste is lithium hydride contaminated with depleted uranium.

Reactivity of the water-reactive wastes is neutralized with an atmosphere of humid nitrogen, which prevents the formation of an explosive mixture of hydrogen and air. When we adjust the temperature of the nitrogen and the humidifier, the nitrogen can be more or less humid, and the rate of reaction can be adjusted and controlled. Los Alamos has investigated the rates of reaction of lithium hydride as a function of the temperature and humidity, and, as anticipated, they increase with increasing temperature and humidity. Los Alamos will investigate other variables. For example, the nitrogen flow will be optimized to conserve nitrogen and yet keep the reaction rates high. Reaction rates will be determined for various forms of lithium waste, from small chips to powder. Bench work will lead to the design of a skid-mounted process for treating wastes. Other water-reactive wastes will also be investigated.

INTRODUCTION

Water-reactive compounds react with water with generation of hydrogen. The reaction is exothermic and sometimes extremely rapid. Hydrogen may ignite or even form an explosive mixture. To comply with the Resource Recovery and Conservation Act (RCRA), the reactivity must be neutralized before land-disposal of the water-reactive wastes.

Los Alamos National Laboratory, as well as other U.S. Department of Energy (DOE) facilities, has various radioactively contaminated water-reactive wastes. The most abundant is lithium hydride. Other wastes include magnesium, sodium, calcium, and some finely divided metals.

The reaction of lithium hydride with water is

$$LiH + H_2O \text{ --> } LiOH + H_2 \qquad (1)$$

A treatment to neutralize lithium hydride reactivity has been tested based on controlled hydration, according to reaction 1, with a humid atmosphere of nitrogen. Nitrogen prevents formation of a flammable or explosive mixture in the reactor. Outside the reactor, the nitrogen-hydrogen mixture can be diluted quickly with air to well below the flammability limit.

The main objective of this program, run at bench scale, was to obtain engineering data necessary for the design of a pilot plant to be tested on the real waste.

The lithium hydroxide formed during reaction 1 is caustic and must be neutralized to comply with RCRA regulations. The radioactive component must also be considered for disposal, for example by immobilization (cementation) of the waste. These steps have not been included in this study.

EXPERIMENTAL SETUP

Figure 1 shows the experimental setup. The nitrogen flow rate is measured through a flow meter. The nitrogen gas enters and bubbles through a humidifier--a metal cylinder filled with glass beads--immersed in a water bath maintained at a constant temperature. The influence of water concentration in the gas stream (humidity) can be studied by changing the humidifier temperature. The humidity can be calculated by the weight loss of the humidifier.

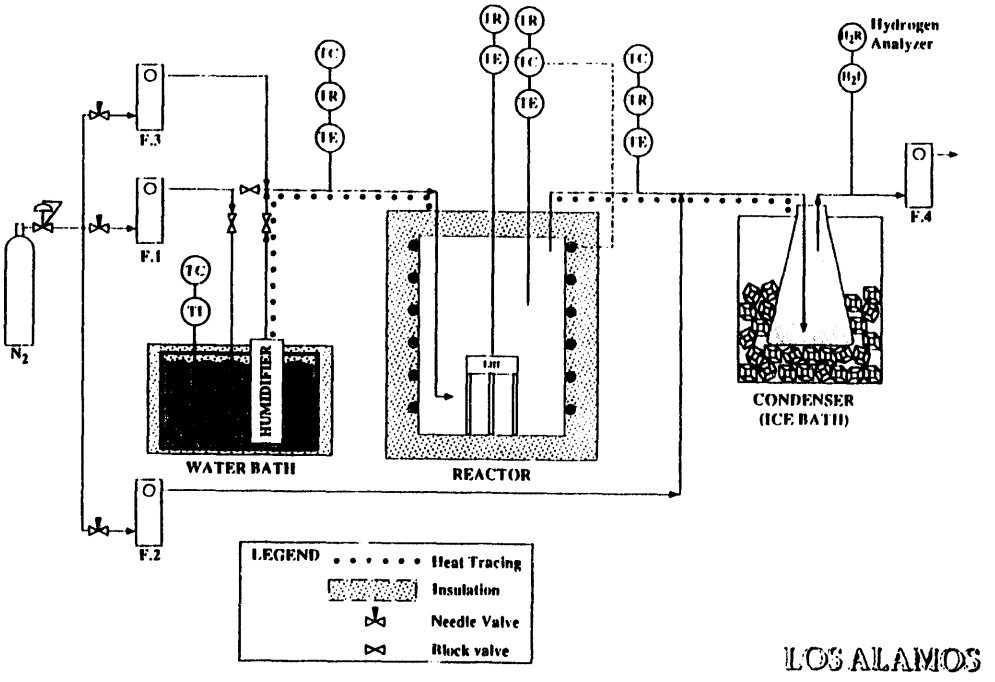

Figure 1. Experimental setup.

Humid nitrogen then passes through the reactor. To prevent condensation, the tubing to the reactor and the reactor itself are maintained at a temperature higher than that of the humidifier, usually 5° C higher. Lithium hydride is placed in a ceramic crucible inside the reactor. A thermocouple immersed in the lithium hydride detects temperature changes.

The gas exiting the reactor goes through a hydrogen analyzer. The tubing to the analyzer is maintained at a temperature sufficient to prevent condensation. However, for experiments at high temperature that could damage the analyzer, the gas is dehumidified and cooled in an ice-cold moisture trap. Also, when hydrogen concentration exceeds the analyzer upper detection limit of 4%, the gas exiting the reactor is diluted with a known flow of nitrogen.

Finally, the gas passes through a flow meter which, by comparison with the inlet flow meter, indicates the presence of a substantial leak.

INFLUENCE OF GAS HUMIDITY

Introduction

The influence of gas humidity on the kinetics of hydration of lithium hydride was studied by running the humidifier at different temperatures. However, to prevent condensation, the humid gas in the reactor must be maintained at a temperature slightly higher than that of the humidifier, typically 5 ° C higher. Also, the reaction is quite exothermic, and the temperature of lithium hydride increases, sometimes substantially. Consequently, both moisture concentration and temperature of reaction changed simultaneously. The influence of temperature of reaction at constant humidity was investigated later in the program.

Hydrogen evolution rate was determined from its concentration in the exiting gas. An example of a recording of hydrogen concentration with time is shown in Fig. 2.

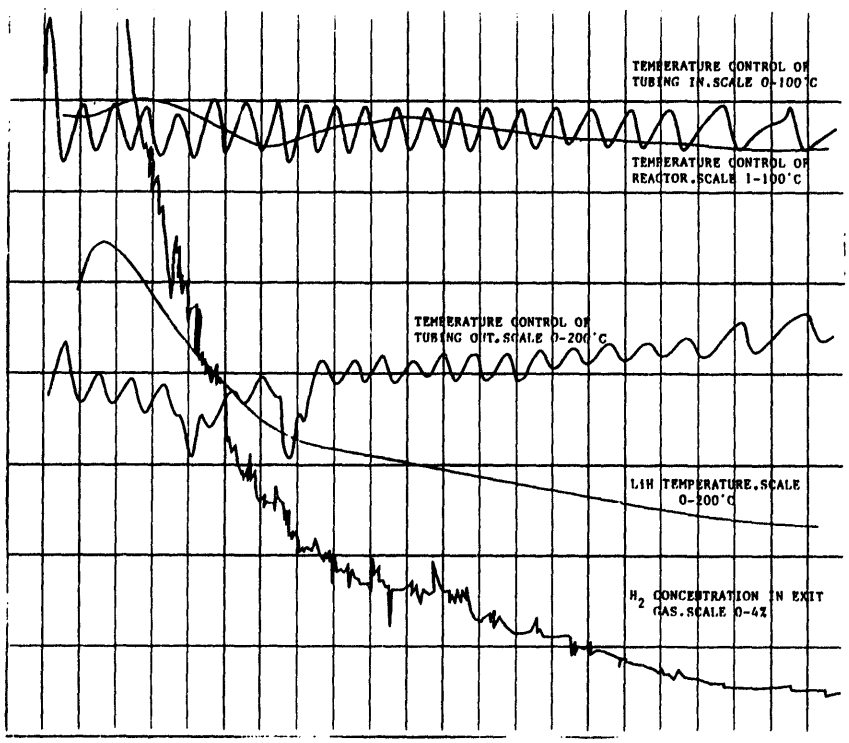

Figure 2. Recording for Test 16 (Humidifier Temperature 80.6

Test Results

Instant reaction rate versus test duration. For the design of the equipment to neutralize lithium hydride, the kinetics of the reaction is important. The kinetics is measured through the rate of hydrogen evolution.

Knowing the instant reaction rate permits calculating evolution at each point in time and the dilution of the reactor's exit gas stream necessary to keep hydrogen concentration below the flammability limit of 4% (and therefore below the explosive limit). Or, conversely, it permits adjusting operating conditions to stay below this limit at constant dilution.

The instant reaction rate may be a function only of the surface area of the unreacted lithium hydride, or it may be affected by the accumulation of a semi-impervious layer of hydroxide as the reaction proceeds. It

may also vary with the humidity, temperature, gas retention time, etc. If a relationship between reaction rate and these variables can be determined, the equipment can be designed to treat larger quantities of lithium hydride.

The average reaction rate over the duration of treatment is another important factor. It indicates whether treatment can be effected in one shift or what conditions to use to complete treatment in a given period of time. The duration of treatment is somewhat imprecise because hydrogen evolution at the end of the test is very low. To compare tests, it is more accurate to determine, for example, the time required for evolution of 80% of the total volume of hydrogen.

Calculation of the instant reaction rate. A model of hydrogen evolution has been made. It assumes that, for a given set of operating conditions, the hydrogen evolution rate with time is a function only of the surface area of unreacted lithium hydride. With this assumption, the hydrogen generation rate, for example in liter/minute/gram, is given by an equation

$$R = ak(1\text{-}bkt)^2 \tag{2}$$

where a and b are constants that have been determined; t is the time; and k is the reaction rate per unit of time and surface area. With the assumption of this model, k is a constant.

The cumulative volume of hydrogen, V_c with time is given by

$$V_c = c\left[1\text{-}(1\text{-}dkt)^3\right] \tag{3}$$

where c and d are constants. V_c has been experimentally determined, which permits calculating k as e and f are constants and t is time.

Experimental determination of the instant reaction. Tests were run at various humidifier temperatures. These tests show a strong influence of the humidifier temperature on the instant volume of hydrogen generated and the time required to complete the reaction. This effect is illustrated in Figs. 3 and 4 for three selected temperatures. It is obvious from the curves in the figures that the kinetics of the reaction is greatly increased by higher temperature and humidity.

The instant reaction rate was calculated at different times for each test. The rate k is calculated from the theoretical hydrogen volume of 3 L/g of LiH at room temperature.

Figure 5 shows the relationship between the reaction rate and the humidity content of the gas. Humidity is given as the percentage by volume of the humid gas that is water vapor.

Data evaluation. Figure 5, which is on a semilogarithmic scale, shows a relatively linear relationship. The points do not line up better for several reasons.

- The product of hydration is a function of the temperature. As mentioned previously, humidity was increased by increasing the humidifier temperature, and hydration also had to be done at a higher temperature to prevent condensation. Figure 6 shows the hydration ratio--the weight ratio of hydrated lithium hydride to the starting weight--as a function of the temperature. At about 80° C and above, it is close to the theoretical ratio of 3.0 for LiOH. Between 35° C and 70° C, the ratio falls between LiOH, H_2O (5.25) and LiOH, 0.5 H_2O (4.1). During the test, the lithium hydride temperature increases substantially for some time because of the exorthermicity of the reaction. For example, Fig. 7 shows the lithium hydride temperature for a test run at a

reactor temperature of 53° C. It increases to approximately 60° C for about 100 min. It is possible that the hydration product is a mixture of LiOH, H_2O, and LiOH, although no positive identification (such as by x-ray diffraction) was made. Typically, the high-temperature product of hydration was dry and grainy, while low-temperature products were deliquescent. It is believed that below 35° C, the reaction rate was too slow, and complete hydration was not reached.

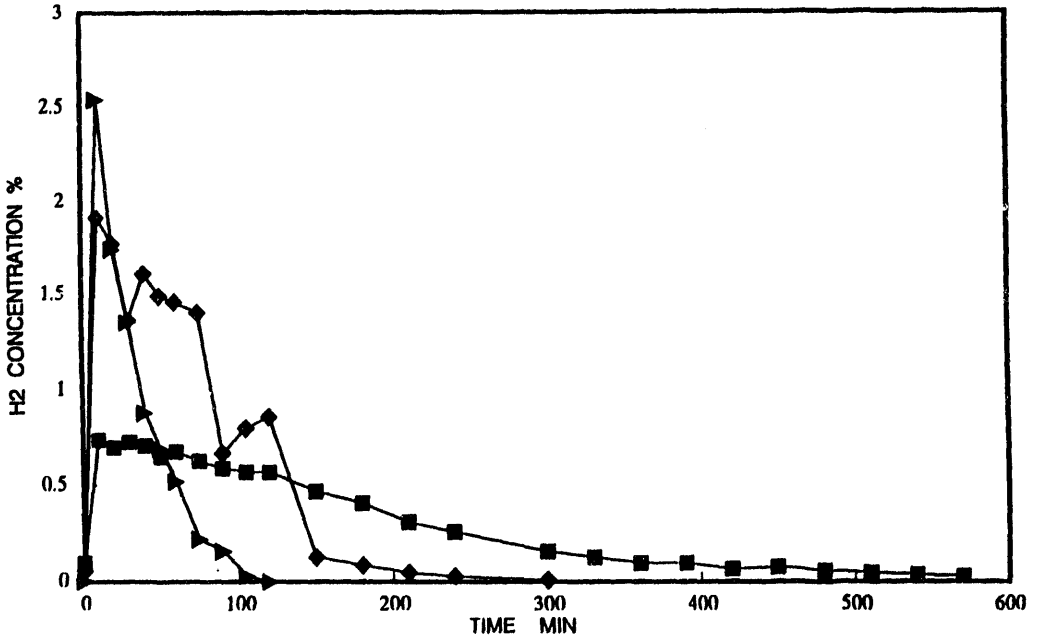

Figure 3. Hydrogen concentrations vs. time. Test #6, 10 & 21.
Humidifier temp °C (36.1, 69.4 & 80.6) respectively.

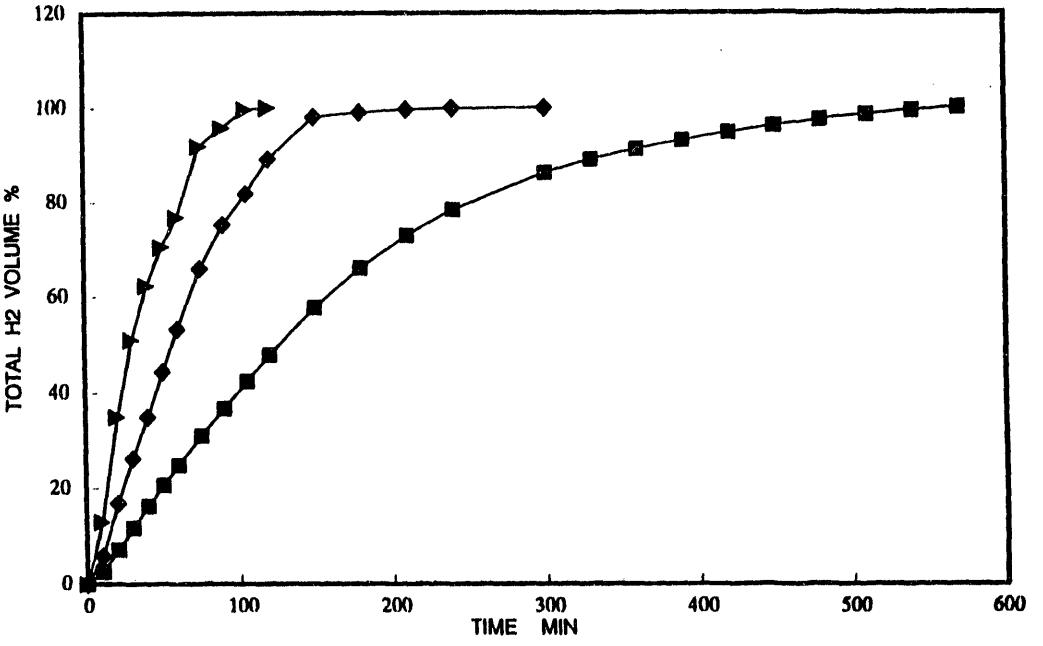

Figure 4. % Total H O volume vs. time. Test #6, 10 & 21.
Humidifier temp °C (36.1, 69.4 & 80.6) respectively.

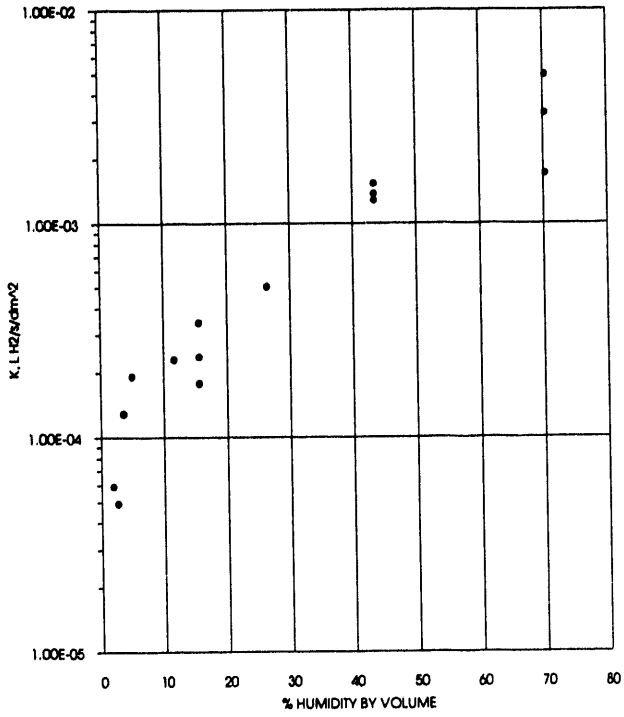

Figure 5. K vs. % humidity.

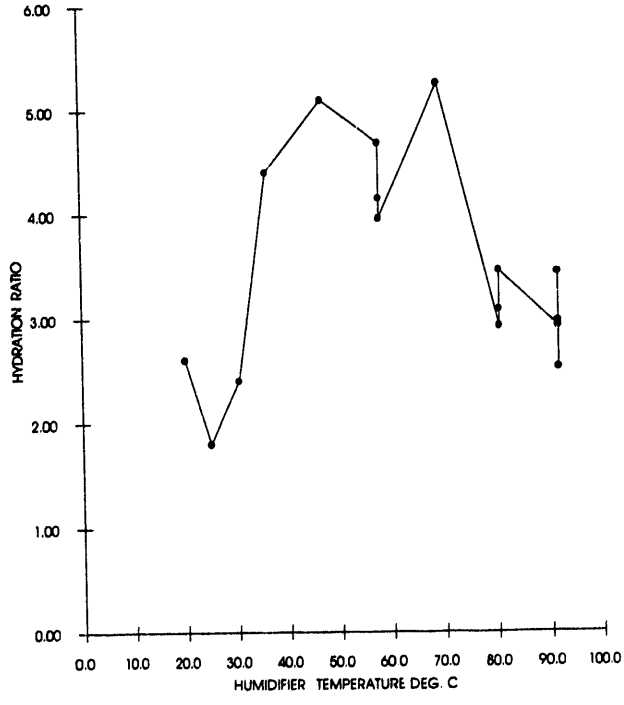

Figure 6. Hydration ratio vs. humidifier temperature. Tests #2-24.

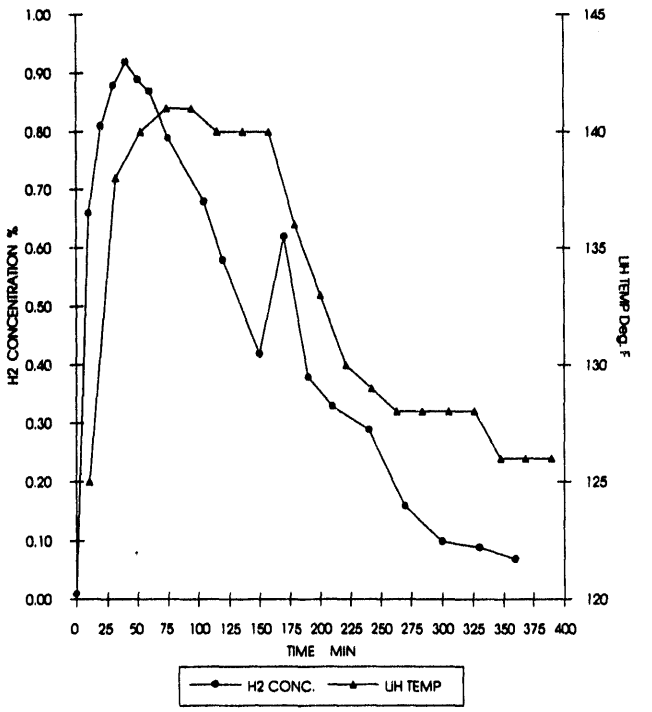

Figure 7. Hydrogen concentration/LiH temperature vs. time. Test #8. Humidifier temperature: 47°C.

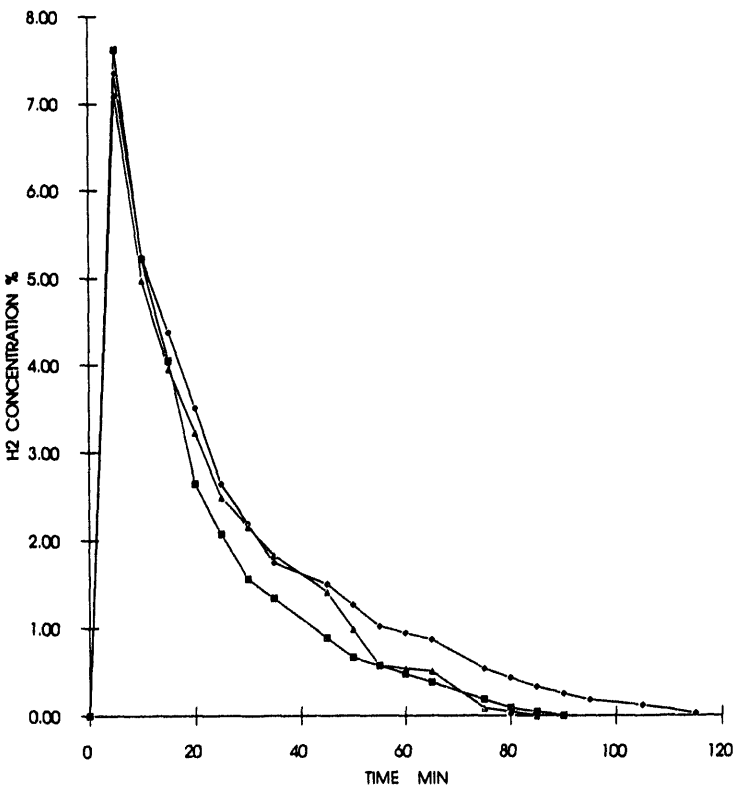

Figure 8. Reproducibility of H_2 evolution. Tests #16, 20 & 21. Humidifier temp. at 80.6°C.

- Most tests were fairly reproducible. For example, Fig. 8 shows three tests run at 80.6° C. However, tests run with the humidities at near boiling were more erratic. Tests at room temperature were too slow to be completed in a day's time.

- The calculation of the rate of reaction assumed a single particle size. Under the microscope, it is obvious that there is a relatively wide range of sizes. The sample used for the test was quite small (0.5 g), and differences in size distribution from one test to the next are likely.

- Drifting of the hydrogen analyzer calibration was fairly common.

CONCLUSION

The influence of gas humidity on the reaction rate with lithium hydride was determined and can be used for preliminary treatment equipment design. To prevent formation of a deliquescent compound (which could impede the reaction for large quantities of chunky lithium hydride) and have a relatively rapid reaction rate, it was decided to run further tests at 80° C.

More accurate values of the reaction rate will be determined by using well-defined screen sizes as well as chunks of lithium hydride. This will also permit verifying the assumption that the reaction rate is a function only of the surface area when other conditions are kept constant.

Other tests will be conducted to study the influence of reactor temperature above the minimum required for a given humidity level, and to attempt to decrease nitrogen consumption, to study other water-reactive wastes.

THE ECO LOGIC PROCESS

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ABSTRACT. ECO LOGIC has developed a high-efficiency gas-phase chemical reduction process for the destruction of hazardous organic wastes. The process uses hydrogen and water at 900°C and ambient pressure to chemically reduce chlorinated organic contaminants to methane and hydrogen chloride. The process was recently demonstrated at pilot scale for the U.S. Environmental Protection Agency's Superfund Innovation Technology Evaluation Program in Bay City, Michigan, processing polychlorinated biphenyl (PCB) contaminated water, oil and soil. These tests showed a destruction removal efficiency of 99.9999% for PCBs for liquids and gases injected into the reactor. The thermal desorption unit used to pre-process soils achieved a desorption efficiency of 99.9% for PCBs and higher efficiencies for more volatile compounds. Product gas from the process is a mixture of hydrogen, methane and carbon monoxide which can be compressed and stored for analysis prior to use as a fuel within the process. The technology offers owners of low=level radioactive mixed wastes a high-efficiency alternative to incineration with the potential to demonstrate effective partitioning prior to any air emissions occurring.

INTRODUCTION

Since 1986, research has been conducted at ELI Eco Logic International Inc. (herein referred to as ECO LOGIC), with the aim of developing a new technology for destroying aqueous organic wastes, such as contaminated harbour sediments, landfill soil and leachates, and lagoon sludges. The goal was a commercially-viable chemical process that could deal with these watery wastes and also process stored wastes (e.g. contaminated soils, solvents, oils, industrial wastes, pesticides and chemical warfare agents). Other companies and agencies at that time were focusing their efforts primarily on incineration, and were investigating a variety of pre-destruction cleaning or dewatering processes to deal with the problem of aqueous wastes. The process described in this paper was developed with a view to avoiding the expense and technical drawbacks of incinerators, while still providing high destruction efficiencies and waste volume capabilities.

A lab-scale process unit was constructed in 1988 and tested extensively. Based on the results of these tests, it was decided to construct a mobile pilot-scale unit that could be used for further testing and ultimately for small commercial waste processing operations. The pilot-scale plant was completed and commissioned in 1991. It was taken through a preliminary round of tests at Hamilton Harbour, Ontario, where the waste processed was coal-tar-contaminated harbour sediment. In 1992, the same unit was taken through a second round of tests as part of the U.S. Environmental Protection Agency (EPA) Superfund Innovation Technology Evaluation (SITE) program in Bay City, Michigan. In those tests, the pilot-scale unit processed polychlorinated biphenyls (PCBs) in aqueous, organic and soil matrices. This paper describes the process reactions and the pilot-scale process unit, and presents the results of pilot-scale testing thus far.

PROCESS CHEMISTRY

The process involves the reduction of organic compounds by hydrogen at temperatures of 850°C or higher.

The system's product gas consists essentially of hydrogen, methane, ethane and trace concentrations of benzene and other polyaromatic hydrocarbons (PAHs). For chlorinated organic compounds, such as PCBs, hydrogen chloride (HCl) also is produced, and is scrubbed out in a caustic scrubber downstream of the process reactor.

Figure 1 summarizes the reactions for the destruction of PCBs, dioxins and PAHs. All reactions in the process are reductive, with the exception of the water-shift reaction. However, this step is nonetheless useful, because it permits the partial recovery and re-use of expensive hydrogen. The overall reaction is enhanced by the presence of water, which acts as a reducing agent and a source of hydrogen. Consequently, aqueous wastes can actually be processed more cheaply than non-aqueous wastes, as opposed to incinerators, in which the presence of water drives up processing costs significantly.

The essential difference between the ECO LOGIC Process and incineration is that the overall reaction is reductive rather than oxidative. Air is excluded from the process system. Consequently, the chances of forming dioxins or furans, which can be products of incomplete combustion of PCBs and some PAHs, are essentially nil. The ECO LOGIC reactor can destroy dioxins and furans just as easily as PCBs.

THE PILOT-SCALE PROCESS UNIT

Figure 2 is a schematic of the reactor where the waste compounds are reduced. The various input streams are injected via several ports mounted tangentially near the top of the reactor. Special nozzles are used to atomize liquid wastes, in order to accelerate liquid vaporization. The gas mixture swirls around a central ceramic-coated steel tube, and is heated on the way by 18 vertical silicon carbide electric heating elements. By the time it reaches the bottom of the reactor, the gas mixture has reached a temperature of at least 850°C. Some particulates initially present in the waste drop out of the reactor bottom and are collected in a grit box. Finer particulates flow up the ceramic tube, into the exit elbow and through the retention zone. The process reactions take place from the bottom of the ceramic tube onwards, and take less than one second to complete.

Figure 3 is a process schematic of the entire pilot-scale system, including the reactor. Most of the components of the pilot-scale system are mounted on two standard drop-deck highway trailers. Hydrogen (H_2) and recirculated product gas are preheated in the recirculation gas heater, which consists of two propane-fired single-ended radiant tube heaters. The recirculation gas flowrate varies with the waste type and concentration, up to a maximum of 95% of the product gas. Nitrogen (N_2) is used to purge the entire assemblage prior to waste processing and following the discontinuation of processing.

Waste enters the reactor via three routes, depending on whether it is watery waste, oily waste, or solid waste. Watery waste is preheated in a vaporizer using steam from a boiler. The contaminated steam from the vaporizer is metered into the reactor at a rate determined by the process control system. Hot contaminated liquid exits the bottom of the vaporizer at a controlled flowrate and enters the reactor through an atomizing nozzle. Oily waste can be metered into the same line using a peristaltic pump.

Solid wastes such as soil or decanted sediment are decontaminated in a thermal desorption unit (TDU) with the contaminants being sent to the reactor through a separate port. The internal workings of the TDU are designed to vaporize all water and organic contaminants in the waste soil/sediment while mechanically working them into as fine a mixture as possible. The water vapor and organic contaminants are swept into the reactor by a sidestream of scrubbed recirculation gas.

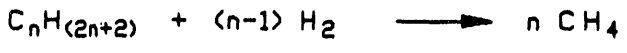
PCB molecule & hydrogen react to produce benzene & hydrogen chloride.

Dioxin molecule & hydrogen react to produce benzene, hydrogen chloride & water.

PAH molecule & hydrogen react to produce benzene & ethylene.

Benzene & hydrogen react to produce methane.

Ethylene & hydrogen react to produce methane.



Hydrocarbons & hydrogen react to produce methane.

WATER SHIFT REACTION

Methane & water react to produce carbon monoxide & hydrogen.

Figure 1. ECO LOGIC process reactions.

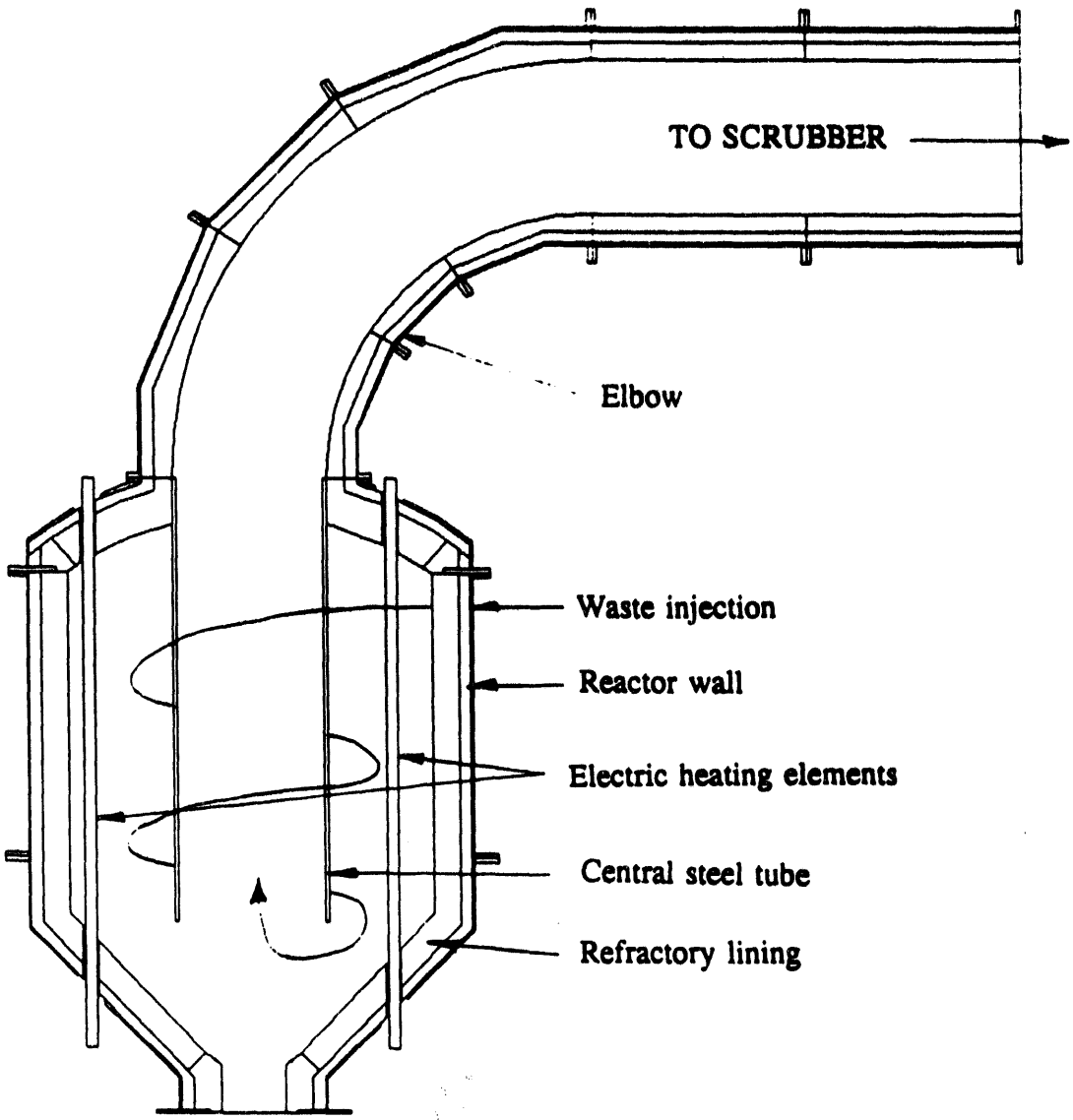
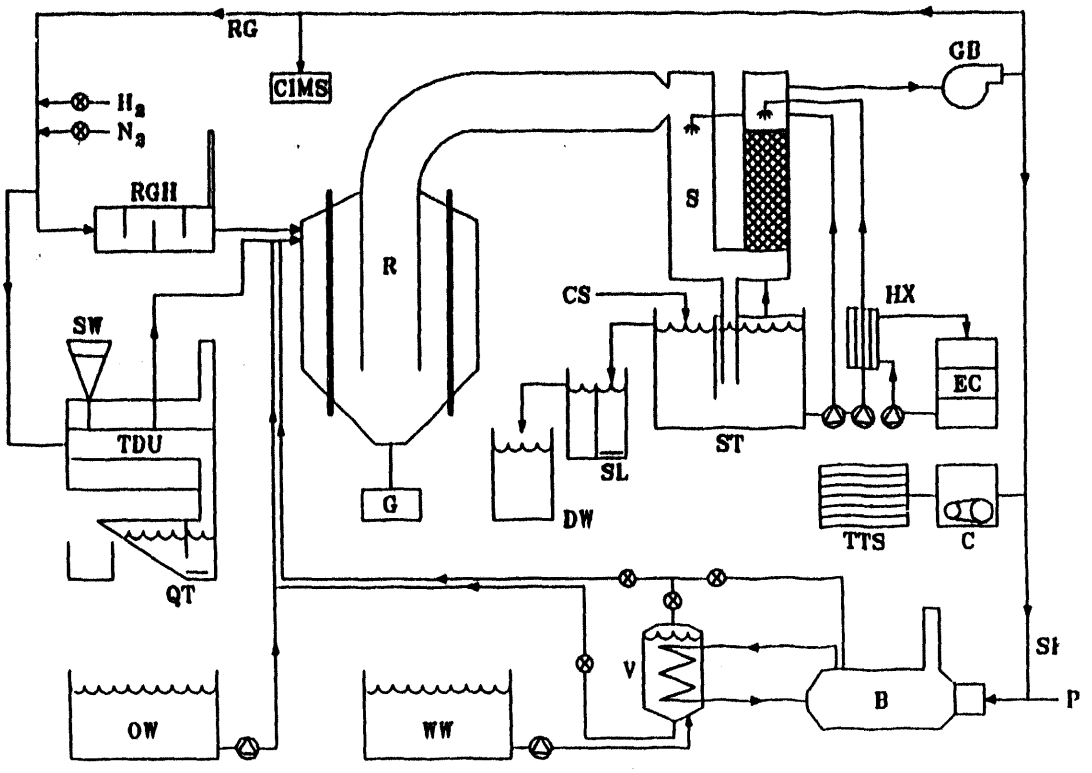


Figure 2. Pilot-scale process reactor.



Boiler		R	Reactor
Compressor		RG	Recirculation Gas
Chemical Ionization Mass Spectrometer		RGH	Recirculation Gas Heater
Caustic Soda (NaOH)		S	Scrubber
Decant Water Tank		SF	Supplementary Fuel (Product Gas)
Evaporative Cooler		SL	Sludge Tank
Grit Collection Box		ST	Scrubber Tank
Gas Booster Fan		SW	Solid Waste
Heat Exchanger		TDU	Thermal Desorption Unit
Oily Waste		TTS	Tube Trailer Storage
Propane		V	Vaporizer
Quench Tank		WW	Watery Waste

Figure 3. Pilot-scale process unit schematic.

The product gas leaving the reactor is scrubbed in a caustic scrubber to remove water, heat, fine particulates, HCl and any other acid gases that may have formed in the reactor. The scrubber water is recirculated from the scrubber tank to sprayers in the first leg of the scrubber and to a polypropylene media bed in the second leg. Sodium hydroxide (NaOH) is added periodically to maintain a scrubber water pH of 9. The heat absorbed by the scrubber water is removed by a plate-plate heat exchanger and evaporative cooler. By the end of the second leg, the product gas temperature has been cooled to approximately 35°C. It is drawn out of the scrubber by a gas booster fan.

The dirty scrubber water from the two scrubber legs returns to the scrubber through a drop-tube that extends well below the water surface. This acts as a seal against air infiltration and as an emergency pressure relief mechanism. Short-term pressure surges can cause gas to exit the bottom of this tube, so one-half of the scrubber tank is partitioned and covered to prevent release. A check valve allows the gas to re-enter the system once the pressure returns to normal. The system normally operates within 10 inches water gauge (0.36 psig) of atmospheric pressure.

As waste is processed through the system, water condenses in the scrubber tank and overflows to a sludge settling tank and then to a decant water tank. The scrubber tank is agitated with a mixer to prevent sludge sedimentation. Decant water is the primary effluent, and after pH balancing, is suitable for sewer disposal. The sludge can be disposed of by adding it to the solid waste being processed in the TDU.

The cooled and scrubbed product gas is a clean dry mixture of hydrogen, methane, carbon monoxide, and other light hydrocarbons. As earlier indicated, most of the gas is reheated and recirculated back into the reactor, in order to maintain a high concentration of hydrogen in the reactor. A sidestream is drawn off for on-line sampling. Sidestreams can also go to the TDU as a sweep gas, to the boiler for consumption as supplementary fuel, or to a compressor for storage under pressure in a tube trailer.

The compression and storage system is only used when a high-strength organic waste is being processed, such as PCB askarel fluid. The amount of methane generated from processing high-strength waste is greater than that which the boiler can accept as supplementary fuel. Storage of the product gas under pressure permits the analysis of large batches of gas prior to using the gas as fuel and allows the operation of the system in a "stackless" mode. Potential applications for the stored product gas include heating the TDU, steam reformation for optimum hydrogen recovery, and steam/electricity generation.
Throughout waste processing operations, the product gas is sampled real-time using a chemical ionization mass spectrometer. This analyser is capable of accurately monitoring up to 10 organic compounds every few seconds at concentrations ranging from g/kg levels down as low as µg/kg levels. It is used as part of the ECO LOGIC process to monitor the concentration of certain compounds indicative of the system's destruction efficiency. The compounds selected for monitoring depend on the waste being processed. For example, during PCB processing, monochlorobenzene is typically monitored as an indicator of destruction efficiency. Low levels of this more volatile compound indicate that destruction of the PCBs is proceeding to completion. A sudden increase in the monochlorobenzene concentration is used to trigger an alarm in the process control system, and the exceedance of a preset threshold is used to automatically put the waste destruction system into a 100% recirculation mode, until the required destruction efficiency is re-attained.

TESTING

The pilot-scale process plant was tested for the first time at Hamilton Harbour, Ontario in 1991. The waste processed during those tests was harbour sediment contaminated with coal-tar at concentrations of up to 300 g/kg (dry weight basis). Destruction Removal Efficiencies (DREs) of 99.99999% were calculated (Table 1), based on the total organic input and the PAHs analysed in the stack emissions (1). During one test, the liquid waste input was spiked with PCBs to create a waste with a PCB concentration of 500 mg/kg. The concentration of PCBs in the air emissions, liquid effluent and processed solids were below the detection

limits for each, respectively. Based on the detection limits for the stack sampling trains, a PCB DRE of at least 99.9999% was achieved.

Table 1. Hamilton Harbour pilot-scale test results.

Run	Target Analytes	Conc. in Waste (mg/kg)	Decant Water Conc. (μg/kg)	Grit Conc. (mg/kg)	Sludge Conc. (mg/kg)	Stack Gas Conc. (μg/kg)	DRE (%)
P1	PAHs	21,000	483	1.67	32.8	0.27	99.9999
P2	PAHs	30,000	680	7.76	56.1	0.23	99.9999
P3	PAHs	30,000	423	0.37	4.3	0.14	99.9999
P4	PCBs	500	ND	ND	ND	ND	99.9999

DRE = (Total Input - Stack Emissions)/(Total Input)
ND - Non-Detect

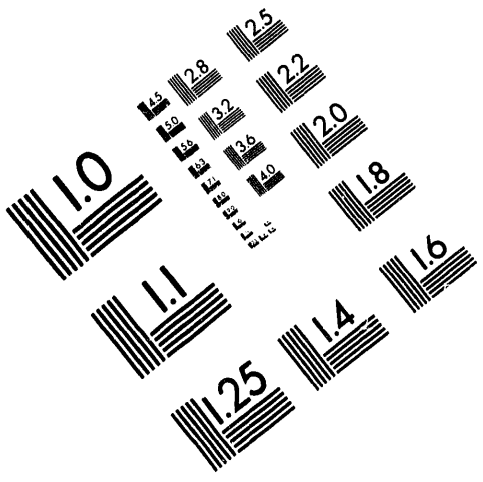
A second round of tests of the pilot-scale unit was conducted in 1992 in Bay City, Michigan as part of the EPA's SITE program. The wastes processed included oily PCB-contaminated water, high-strength PCB oil, and PCB-contaminated soil. Triplicate test runs were conducted for each waste type. Unofficial results obtained on-site from ECO LOGIC's mobile lab are shown in Table 2. The results for the first two series of tests (PCB-contaminated water, high-strength PCB oil) have been confirmed by the EPA (2). The official USEPA results are expected to be available soon in the form of a SITE Program Project Bulletin, an Applications Analysis Report and a Technology Evaluation Report.

Table 2. USEPA SITE Program - Results Summary

Contaminant	Media	Volume	Concentration	
			Initial (mg/kg)	Final (mg/kg)
PCBs	water/oil	0.5 tonne	4,000	< 0.0001
PCBs	oil	100 gals.	400,000	< 0.0001
PCBs	soil	1 tonne	1,000	0.6000*

* Second test run.

The first set of three test runs processed contaminated groundwater and 400 g/kg PCB oil in a 100:1 ratio. The oil was injected directly into the reactor and the contaminated groundwater was injected as steam and hot water. The sum of waste inputs to the reactor gave a bulk input concentration of 4000 mg/kg PCBs. The scrubber water, which was recirculated throughout each 6-hr. test, had a concentration of less than 0.1 μg/kg PCBs at the end of each test.



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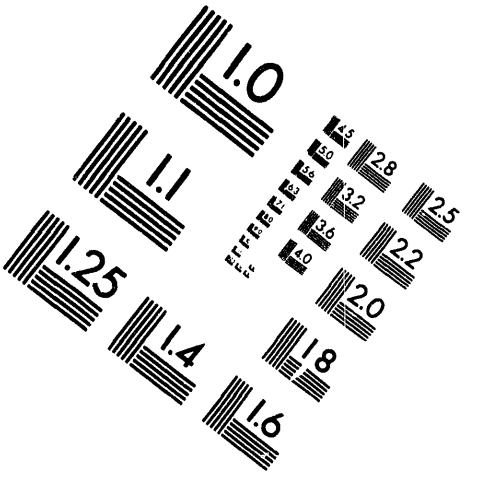

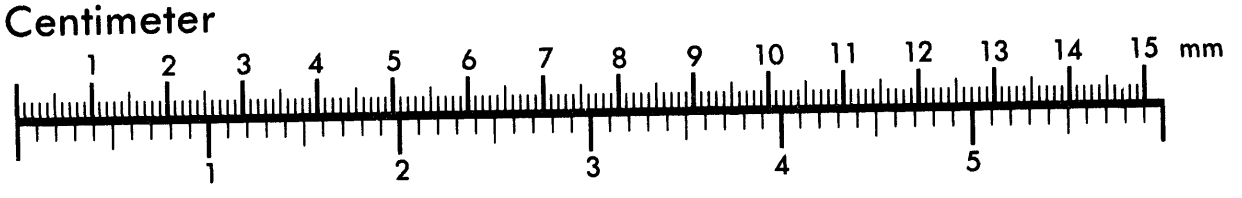

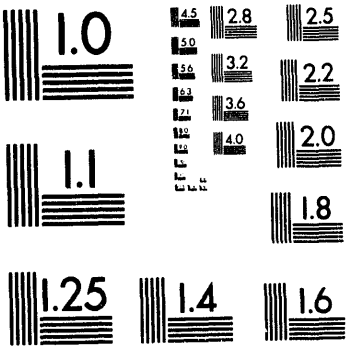

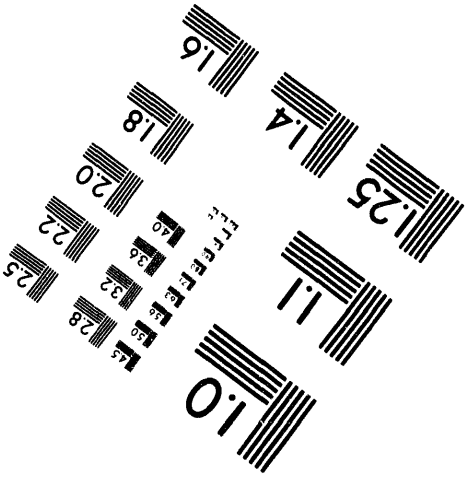

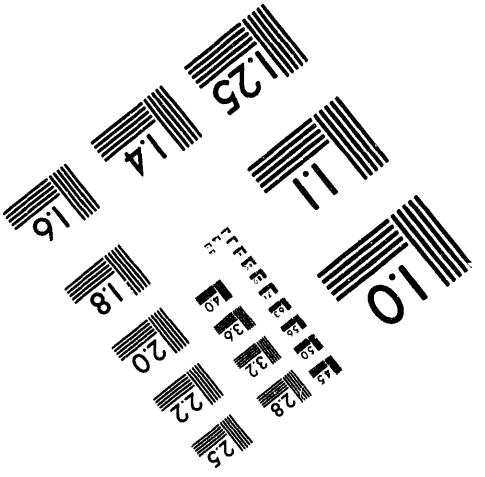

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The second set of three test runs processed high-strength 400 g/kg PCB oil directly at approximately the same rate as the contaminated water. The product gas generated for these 2-hour tests was compressed and stored in a tube trailer. The scrubber water again had a concentration of less than 0.1 µg/kg PCBs at the end of each test. After waste processing, the stored gas was directed to the boiler for about 24 hrs., and stack testing by the EPA sub-contractor was conducted.

The third set of test runs was delayed until construction and commissioning of the new TDU was completed. During the first TDU test, contaminated soil from the landfill containing more than 1000 mg/kg PCBs was processed and a desorption removal efficiency of 96% was achieved. This result was encouraging for a first run, but the desorbed soil was still above disposal guidelines. The waste soil residence time inside the TDU was increased for the second run, and a desorption removal efficiency of 99.9% was achieved. Due to Toxic Substance Control Act permit restrictions, only two runs were done for the third test condition. It should be noted that the performance of the TDU is independent of the destruction process. The reactor destruction efficiencies for the desorbed contaminants were high for both TDU runs.

The fourth test condition was a 72-hr. performance test aimed at demonstrating the continuous operation capabilities of the ECO LOGIC process. The equipment operated perfectly and the 72-hr. test was concluded successfully.

FUTURE WORK

Future work on the development of the ECO LOGIC process currently focuses on the following areas:

- The design and construction of a full-scale mobile process unit, with an associated product gas compression-and-storage system. An associated steam reformer is also being planned, to optimize the recovery and re-use of hydrogen from the methane in the product gas.
- The modification and further development of the TDU. Various components of this unit are being re-evaluated and re-designed to improve its soil desorption and material handling capabilities.
- The design and construction of a Sequence Batch Vaporizer (SBV). This new unit will be supplementary to the full-scale process unit. Its purpose will be to facilitate the processing of stored wastes and contaminated solids which cannot be readily injected directly into the reactor or processed in the TDU. The SBV will consist of two large sealable chambers, through which heated recirculation gas will sweep, vaporizing all organic contaminants and carrying them away to the reactor. Batches of waste will be loaded alternately into each chamber of the SBV and removed once decontaminated. Typical wastes suited to processing in the SBV include contaminated large pieces of equipment (such as electrical transformer carcasses), and drummed organic material (such as obsolete pesticides and chemical warfare agents).
- Lab-scale and pilot-scale testing with mixed wastes. This will initially involve processing simulated mixed waste at lab-scale. Depending on the lab-scale results, further tests with real mixed waste will be conducted at a licenced radioactive waste disposal site. The real mixed waste tests could be at either lab-scale or pilot-scale.

ACKNOWLEDGEMENTS - ECO LOGIC is grateful to the EPA, the Canadian Department of National Defence, Environment Canada, the Ontario Ministry of Energy and the Environment, and the Canadian National Research Council for funding and support during the development of the ECO LOGIC process.

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CHAPTER 8

Laboratory and Analytical Issues

NEEDED SAMPLING AND ANALYTICAL METHODS FOR THE DOCUMENT: "DOE METHODS FOR EVALUATING ENVIRONMENTAL AND WASTE MANAGEMENT SAMPLES"

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ABSTRACT. The document "DOE Methods for Evaluating Environmental and Waste Management Samples" (DOE Methods) contains methods that give guidance for sampling and analyzing mixed waste and environmental samples from Department of Energy (DOE) sites. The document was first issued in October, 1992, and is updated every six months. New sampling and analytical methods that have successfully completed the DOE Methods review process are added with each update. Identification of methods needed to address relevant concerns to DOE and that are not included in existing standard methods is an important part of this process. Categories in the areas of organic, inorganic, radiochemistry, miscellaneous analytical, and sampling have been classified. These categories identify types of methods needed to complete DOE Methods. Some categories show gaps that are not addressed by existing standard methods. The method needs have been prioritized to emphasize sampling and analysis in radioactive waste and environmental matrices. Based on an evaluation of over 1,000 procedures compiled from sites from across the DOE complex and currently in the DOE Compendium Procedures Database, several hundred specific organic, inorganic, radiochemistry, and sampling method needs for future inclusion in DOE Methods have been identified. The needs lists depicted in this paper are presented as guidance to DOE, DOE contractors, and commercial contractors interested in submitting methods for consideration for possible inclusion in DOE Methods. The authors encourage feedback from readers on the content of the lists. All feedback will be given serious consideration in future updates of the needs lists.

BACKGROUND

First released by the Department of Energy (DOE) in October, 1992 (1), DOE Methods contains guidance and validated methods for use by the DOE and DOE contractor laboratories (2,3) with emphasis on the characterization of radioactive waste and environmental samples of interest within DOE. The first issue contained four methods designed for high-level radioactive waste analysis. The March, 1993 issue contained three new methods and one revised method (4). DOE Methods is a living document where new methods will be continually added, and is reviewed and updated biannually.

The sampling and analytical methods that appear in DOE Methods are either developed for Laboratory Management Division (LMD) or selected from a database containing sampling and analytical methods from across the DOE complex. Similar methods in the database are consolidated, and before being included, the consolidated method is subjected to a review, validation, and approval process. Unique methods meeting certain selection and validation criteria such as quality control (QC) data availability, single or multiple laboratory verification are also being incorporated into DOE Methods. Where applicable to their needs, approved methods are submitted to Environmental Protection Agency (EPA) for evaluation in their methods documents such as SW-846 (5).

Over the past year, and during the conduct of the methods evaluation, consolidation, and review process, method needs have been identified in a number of sampling and analytical areas and conceptualized in the form of the following four areas: sampling, organic analyses, inorganic analyses, and radiochemical analyses. This paper describes these areas of method needs for DOE Methods. At the present time, method needs are those perceived by the authors of this manuscript, as well as other contributors to the DOE methods compendium program. This information is provided to encourage comments that will enhance the accuracy of our perception of DOE environmental restoration and waste management (EM) method needs. Readers are therefore encouraged to send comments regarding their ideas for method needs and possible methods to the authors of this paper for consideration in subsequent updates of the needs lists.

METHOD NEEDS IDENTIFICATION PROCESS

Over the past year, a number of activities and information sources have been used to identify method needs. Activities have included 1) acquisition of methods and 2) use of a database to prioritize and evaluate method submission. Since the middle of FY 1991, Los Alamos National Laboratory (LANL) and Pacific Northwest Laboratory (PNL), through communication networks, have been acquiring procedures from the DOE and DOE contractor analytical laboratories within the DOE complex. Network-received procedures have been transformed into text and image files and stored in a database managed by LANL. To date, well over 1,000 procedures have been entered into the database. In the conduct of these activities, gaps in the scope of the content of procedures in the database have been identified. To develop methods, authors have maintained close contact with laboratories funded by the LMD. They have also used the information describing methods under development to assist in defining the scope of needs lists. Searches of the DOE literature is another avenue currently being explored to identify methods under development across the DOE complex. A developing knowledge of the general activities at DOE sites that require the use of sampling and analysis methodologies in the conduct of EM programs has been helpful to the authors in preparing needs lists. Based on information consolidated from the above process, Tables 1 through 4 (identifying method needs) have been prepared and are summarized below. Readers of these lists are encouraged to provide feedback to the authors on improving the accuracy of these perceived needs.

Sampling

Few methods are available in the regulatory literature that address sampling of radioactive matrices. Although DOE Methods is a guidance, but not a regulatory document, detailed sampling methods are being processed and will soon be included. Initially, these methods will be oriented toward the high-level radioactive waste tanks at Hanford, Savannah River, Oak Ridge, INEL, and other DOE sites. Later, other needs, such as those described in Table 1, will be met. Some sampling method needs include:

Table 1. Sampling Methods Needs List.

Analyte Matrix	High-Level Mixed			Low-Level Mixed				High-Level Radioactive			
	Tank Wastes	Waste Forms	Waste Disposal Sites	Tank Wastes	Waste Forms	Waste Disposal Sites	Monitoring and Surveillance	Tank Wastes	Waste Forms	Waste Disposal Sites	Monitoring and Surveillance
Solids	X[1]	X[4]	X[7]	X[1]	X[4]	X[10,11]	X[15]	X[18]	X[4]	X[7]	X[21]
Liquids	X[2]	X[5]	X[8]	X[2]	X[5]	X[12,13]	X[16]	X[19]	X[5]	X[8]	X[22]
Air	X[3]	X[6]	X[9]	X[3]	X[6]	X[9,14]	X[17]	X[20]	X[20]	X[9]	X[23]

	Low-Level Radioactive				Hazardous		
	Tank Wastes	Waste Forms	Waste Disposal Sites	Monitoring and Surveillance	Tank Wastes	Waste Disposal Sites	Monitoring and Surveillance
Solids	X[18]	X[4]	X[10,11]	X[24]	X[27]	X[30]	X[33]
Liquids	X[19]	X[5]	X[12,13]	X[25]	X[28]	X[31]	X[34]
Air	X[20]	X[6]	X[9,14]	X[26]	X[29]	X[32]	X[35]

X = Needs

Notes:

1. Sampling of saltcake, sludge, and dry calcined materials (high and low pH), limited access (mixed contaminants).
2. Sampling of aqueous and organic layers (high and low pH), limited access.
3. Headspace sampling (radionuclide, inorganic and organic species), limited access.
4. Sampling of vitrified (glass [HLW] or grout [LLW]) materials.
5. Sampling of leachates of vitrified (glass [HLW] and grout LLW]) materials.
6. Sampling gaseous emissions from repository wastes.
7. Soil, sediments and waste (highly modified drilling and unique sampling strategies).
8. Surface water and ground water (highly modified drilling and unique sampling strategies).
9. Modified soil-gas sampling strategies.
10. Soil, sediments, and waste (may require modified drilling and sampling strategies).
11. Solids in drums, likely non-homogeneous (may require modified sampling strategies).
12. Surface and groundwater (may require modified sampling strategies).
13. Miscible/immiscible aqueous/organic liquids in drums (may require modified sampling strategies).
14. Headspace (confined and unconfined) in drums. May require modified headspace sampling strategies.
15. Soils and sediments (may require modification to CERCLA/RCRA sampling procedures.
16. Surface waters and groundwaters (may require modifications to CERCLA/RCRA sampling procedures.
17. Air (may require modification to CERCLA/RCRA sampling procedures).
18. Sampling of saltcake, sludge, and dry calcined materials (high and low pH), limited access, radionuclide and possible metals/inorganic anions.
19. Sampling aqueous layers (high and low pH), limited access, radionuclides and possible metals/inorganic anions.
20. Head space sampling (volatile radionuclide-containing species, metal complexes, etc.).
21. Soils, sediments, food chain materials ,and products (also emergency sampling).
22. Surface water, ground water, food chain products (also emergency sampling).
23. Air sampling (also emergency sampling).
24. Soils, sediment, and waste (may require modified procedures).
25. Surface water and groundwater (may require modified procedures).
26. Soil, gas, and air sampling (may require modified procedures).
27. Above and below ground storage tanks (solvent/fuel sludge materials). Innovative non-standard (non-CERCLA/RCRA) methodologies.
28. Above and below ground storage tanks (solvent, fuels, and chemical mixtures). Innovative non-standard (non-CERCLA/RCRA) methodologies.
29. Above and below ground storage tanks (headspace analysis of organics). Innovative non-standard sampling (non-CERCLA/RCRA) methodologies.
30. Soils, sediments, and wastes including solid materials in drums. Innovative non-standard sampling (non-CERCLA/RCRA) methodologies.
31. Surface and ground waters including liquid materials in drums. Innovative non-standard sampling (non-CERCLA/RCRA) methodologies.
32. Headspace analysis including confined and unconfined headspace in drums. Innovative non-standard sampling (non-CERCLA/RCRA) methodologies.
33. Innovative non-standard (non-CERCLA/RCRA) methodologies for sampling soils and sediments, food chain materials, and products.
34. Innovative non-standard (non-CERCLA/RCRA) methodologies for sampling surface and groundwaters and food chain materials and products.
35. Innovative non-standard (non-CERCLA/RCRA) methodologies for sampling air.

- sampling of saltcake, sludge, and dry calcined materials from waste tanks
- sampling of aqueous and organic layers from waste tanks
- headspace sampling of waste tanks
- sampling of vitrified materials—glass [high-level waste (HLW)] or grout [low-level waste (LLW)]
- sampling of leachates of vitrified materials—glass (HLW) and grout (LLW)
- sampling gaseous emissions from repository wastes
- solids in drums
- miscible/immiscible aqueous/organic liquids in drums
- headspace in drums.

Analytical

Many analytical methods for organic and inorganic analytes are available in standard regulatory documents, such as SW-846 (5) and Contract Laboratory Program (CLP). However, these do not adequately cover the needs of DOE-EM. As a result, various labs within the DOE complex have developed their own procedures to address those concerns. Some specific examples are given in the recent version of DOE Methods (4). Others are suggested in Tables 2 through 4.

Analytical methods for radionuclides are not generally available in standard documents such as American Society for Testing Materials (ASTM) (6,7), SW-846 (5), or CLP. However, methods available from HASL 300 (8) and ASTM (6,7) have been commonly used for measuring environmental levels of radionuclides. DOE Methods supplements and references these documents to expand the resources available for EM activities.

Analytical needs for *DOE Methods* are separated by organic, inorganic, and radiochemistry needs below. In addition to these categories, "miscellaneous" needs are likely to exist, such as those described in SW-846 (5). A specific example is measuring the flammability or other physical properties of radioactive waste. For simplicity, miscellaneous method needs are not described in this document.

Organic

The greatest needs for organic analytical methods are in the analysis of hazardous organic components in radioactive samples. When the levels of radioactivity are small, standard methods may be appropriate. However, as the levels increase, the applicability of these methods tends to diminish. For highly radioactive waste, other hazards, such as ppm levels of acetone, may not be very important unless they interfere with waste treatment processes. However, highly radioactive materials that are also highly hazardous due to the presence of organic components may need to be analyzed for chemical hazards. Detailed method needs are indicated in Table 2. Generally, the needs for organic methods in DOE Methods include those for

- nonvolatile organic compounds such as chelating agents, alkyl phosphates, lubricating oils, etc.
- headspace or soil gas analysis in radioactive environments, e.g., highly toxic vapors, such as phosgene, in tanks, drums, etc.
- standard or novel methods that can be adapted to high activity work, e.g., in hot cells
- use of chemical sensors for specific or class type analysis in in-situ, remote, or hostile environments
- techniques that remove radioactivity from a mixed waste matrix so that standard organic analysis is possible (e.g., selective partitioning including chelation, adsorption, reverse phase, ion exchange, and size exclusion chromatography)

Table 2. Organic Methods Needs List.

Analyte / Matrix	High-Level Radioactive						Low- to Moderate-Level Radioactive					
	Tanks	Disposal Sites[5]	Soil/ Water Monitoring	Field/ Lab Screen	Lab Prep	Lab Analysis	Tanks	Disposal Sites	Soil/ Water Monitoring	Field/ Lab Screen	Lab Prep	Lab Analysis
VOC[1]	X[6,7,8]	X[6,7,8]	X[6,8]	X[6,8,9, 10]	X[7,9,12]	X[7]	X[6,8,14]	X[6,8,14]	X[6,8,14]	X[6,8,9, 10]	X[9,14]	X[14]
Semi-VOC[2]	X[7,8]	X[7,8]	X[8]	X[8,9,10, 11]	X[7,9,11, 13]	X[7,13]	X[8,14]	X[8,14]	X[8,14]	X[8,9,10, 11]	X[9,11,13, 14]	X[13,14]
Non-VOC[3]	X[7,8]	X[7,8]	X[8]	X[8,9,10, 11]	X[7,9,11, 13]	X[7,13]	X[8,14]	X[8,14]	X[8,14]	X[8,9,10, 11]	X[9,11,13, 14]	X[13,14]
TOC, TOX[4]				X[9,10]		X[7,13]				X[9,10]		X[13,14]

	Non-Radioactive				
	Disposal Sites	Soil/ Water Monitoring	Field/ Lab Screen	Lab Prep	Lab Analysis
VOC[1]	X[8]	X[8]	X[8,10,15]	X[15,17]	X[15,16,17]
Semi-VOC[2]	X[8]	X[8]	X[8,10,11,15,16]	X[11,15,16,17]	X[15,16,17]
Non-VOC[3]	X[8]	X[8]	X[8,10,11,15,16]	X[11,15,16,17]	X[15,16,17]
TOC, TOX[4]			X[10]		X[17]

X = Needs

Notes:

1. VOC are volatile organic compounds, including those that are both soluble and relatively insoluble in water.
2. SemiVOC are semivolatile organic compounds.
3. NonVOC are relatively nonvolatile organic compounds such as chelating agents, alkyl phosphates, lubricating oils, etc.
4. TOC=total organic carbon; TOX=total organic halides.
5. Both nominally contained sites (e.g., drums) and uncontained sites.
6. Headspace or soil gas analysis in radioactive environments, e.g., highly toxic vapors, such as phosgene, in tanks, drums, etc.
7. Standard or novel methods that can be adapted to high level work, e.g., in hot cells.
8. Use of chemical sensors for specific or class type analysis in in situ, remote, or hostile environments.
9. Techniques which remove radioactivity from a mixed waste matrix so that standard organic analysis is possible (e.g., selective partitioning including chelation, adsorption, reverse phase, ion exchange, and size exclusion chromatography).
10. Screening methods (enzymatic, chromatographic, spectroscopic) for rapid analysis of organics in hazardous and mixed waste liquids and solids such that sample handling, waste generation, and human exposure are minimized.
11. Extraction procedures to minimize sample volumes, lab waste--e.g., mini-soxhlet, supercritical fluid extraction, solid phase techniques.
12. Purge and trap in a hot cell.
13. Novel methods to overcome problems associated with interferences from mixed waste samples (e.g., alkaline sludges interfere with recovery of acidic compounds; nitrates are reactive.
14. Standard or novel methods that can be adapted to low to medium level work, e.g., in a glove box or protected hood.
15. New methods for non-regulated organics.
16. New methods for polar organics.
17. SW-846 or ASTM methods that are used for low-level or non-radioactive samples. Only significant modification should be included in the compendium.

- screening methods (immunoassay, chromatographic, spectroscopic) for rapid analysis of organics in hazardous and mixed waste liquids and solids such that sample handling, waste generation, and human exposure are minimized
- extraction procedures to minimize sample volumes and lab waste (e.g., mini-soxhlet, supercritical fluid extraction, solid phase techniques)
- novel methods to overcome problems associated with interferences from mixed waste samples (e.g., alkaline sludges interfere with recovery of acidic compounds; nitrates are reactive)
- new methods for polar organics
- field methods.

Inorganic

Similar concerns and needs in the analysis of hazardous organics in radioactive samples exist for organic and inorganic analytes. As the levels of radioactivity increase, the applicability of standard methods is diminished. Highly radioactive materials that are also highly hazardous because inorganic components may need to be analyzed for the inorganic hazards. Detailed method needs are indicated in Table 3. Generally, the needs for inorganic methods in DOE Methods include those for

- standard methods and novel concepts that can be adapted to high level, e.g., hot cell work
- standard methods and novel concepts that are adapted to hot cell work and apply to special inorganic species such as non-hazardous metals that interfere with remediation activities
- new techniques which remove wastes of high levels of radioactivity so that subsequent inorganic analysis is possible
- novel or adapted standard methods for highly radioactive samples for determination of complexed species
- gas or vapor phase determinations in radioactive headspaces (tanks, drums, etc.)
- remote monitoring or novel techniques for field estimation of anions or metals
- pretreatments that remove interfering organic or inorganic species from the desired analytes
- standard methods or novel concepts that can be adapted for protected hood work
- determinative methods for complexed species in mixed wastes, including preconcentration or purification methods
- novel methods that allow for field screening of complexed species in the presence of radiochemical components.

Radiochemistry

Several ASTM and other standard analytical methods for radionuclides have been published (Table 4). In addition, methods are available from the HASL Procedures Manual (6) that have been commonly used for measuring environmental levels of radionuclides. DOE Methods supplements and references these documents to expand the resources available for EM activities. Methods currently available are generally applicable to water, and sometimes to soil matrices (Table 4). Specific needs for DOE Methods include methods for field analysis or laboratory analysis of radionuclides in complex matrices, such as those from Savannah River, INEL, ORNL, or Hanford tanks, or oily matrices. Other specific needs for this document include methods for

- sample preparation for volatile isotopes such as I-129, H-3
- preparation of liquids, solids, and salts for various analytes indicated in Table 4
- isolation of alpha emitters from high-level waste.

Table 3. Inorganic Methods Needs List.

Analyte Matrix	High-Level Radioactive Environs					Moderate Radioactive Environs				
	Tanks	Disposal Sites	Soil/ Water Monitoring	Multiphastic Wastes	Field Analysis Screen	Tanks	Disposal Sites	Soil/ Water Monitoring	Multiphastic Wastes	Field Analysis Screen
Metals	X[4]	X[4]	X[4]	X[4,9,11]	X[10]	X[12]	X[12]	X[16]	X[11,21]	X[20]
Anions	X[4]	X[4]	X[4]	X[4,9,11]	X[10]	X[12]	X[12]	X[16]	X[11,21]	X[20]
Minor Inorganics[1]	X[5]	X[5]	X[5]	X[5]	X[5]	X[13]	X[13]	X[17]	X[17]	X[17]
Pretreatments for Rad Remove	X[6]	X[6]	X[6]	X[6]	X[6]	X[14]	X[14]	X[18]	X[18]	X[22]
Complexed Inorg Species[2]	X[7]	X[7]	X[7]	X[7]	X[7]	X[15]	X[15]	X[19]	X[19]	X[23]
Gasses Vapours[3]	X[8]			X[8]	X[8]	X[8]			X[8]	X[8]

	Low-Level Radioactive Environs				
	Tanks	Disposal Sites	Soil/ Wate Monitoring	Multiphastic Wastes	Field Analysis Screen
Metals		X[25]	X [25]	X[25]	X[26]
Anions		X[25]	X[25]	X[25]	X[26]
Minor Inorganics[1]		X[25]	X[25]	X[25]	X[26]
Pretreatments for Rad Remove					
Complexed Inorg Species[2]		X[25]	X[25]	X[25]	X[26]
Gasses Vapours[3]		X[24]	X[24]	X[24]	X[24]

X = Needs

Notes:

1. Inorganic species that include hydrazine, hydrogen peroxide, aqua ammonia, etc.
2. Organic and inorganic complexants that include a metal nucleus, e.g., ferrocyanide, EDTA complexants.
3. Hydrogen, inert atmospheres, vapor phase inorganics such as ammonia.
4. Standard methods and novel concepts that can be adapted to high level work, e.g., hot cell work.
5. Standard methods and novel concepts that are adapted to hot cell work and apply to special inorganic species.
6. New techniques which relieve wastes of high levels of radioactivity so that subsequent inorganic analysis is possible.
7. Novel or adapted standard methods for highly radioactive samples for determination of complexed species.
8. Gas or vapor phase determinations in radioactive headspaces (tanks, drums, etc.).
9. Determinative methods designed for mixed wastes in hot cell work and site specific methods.
10. Remote monitoring or novel techniques for field estimation of anions or metals.
11. Pretreatments which remove interfering organic or inorganic species from the desired analytes.
12. Standard methods or novel concepts that can be adapted for protected hood work.
13. Novel methods for the special types of inorganics which can be adapted for protected hood work.
14. Radioactive removal techniques that allow standard inorganic methods without contaminating equipment or removes interferences from the matrix.
15. Novel methods for complexed species at intermediate radioactive levels for complexed species.
16. Determinative protected hood methods for inorganics, specific to sites proximate to highly radioactive contamination.
17. Special inorganic methods adapted for environmental (lab or field) applications.
18. Pretreatments to remove interfering radioactivity at moderate levels so that standard methods may be employed.
19. Determinative methods for complexed species in mixed wastes, including preconcentration or purification methods.
20. Specific methods adapted for field screening of moderately radioactive samples for key inorganic constituents.
21. Novel or adapted standard methods designed to be used with mixed wastes, including treatments to remove interfering organic and inorganic species from the matrix.
22. Pretreatments which remove radioactive species so that unprotected field analysis can be done on samples.
23. Novel methods which allow for field screening of complexed species in the presence of radiochemical components.
24. Headspace (drums) or soil/gas measurements for desired inorganic gas or vapor (hydrogen, ammonia, etc.).
25. ASTM or SW-846 methods that are adapted for low-level samples. These may not be amenable to compendium inclusion.
26. Field methods (non-standard or standard) for evaluating DOE sties that have limited radioactive contamination.

Table 4. Radiochemistry Methods Needs List.

Analyte Matrix[1]	Field			Laboratory			
	Soil	Liquid	Tank/ High Level	Soil	Liquid	Tank/ High Level	Organic
Sample Collection	X[2]	X[3]	X				
Sample Preparation				ASTM C[(a)] 999[(b)] 4,5,6		X[7]	X
Screens							
Alpha	X	X		X	EPA 900.0[(c)]	X[8]	X
Beta	X	X		X	ASTM D[(d)] 1943 EPA 900.0 ASTM D 1890	X	X
Gamma (gross)	X	X	X			X	
Gamma (spec)					EPA 901.1		
Ge(Li) or HPG	X	X	X	X	ASTM D 3649	X	X
NaI(Tl)	X	X	X	X	ASTM D 4962	X	
Chemical Separations							
For Alpha Analysis							
Pu				ASTM C 1001	ASTM D 3865	X	
U				ASTM C 1000	EPA 908.0 ASTM D 3972	X	
Th				X	X	X	
Am				X	X	X	
Ra				X	EPA 903.0 EPA 903.1 ASTM D 2460	X	
Po				X	X	X	
Cm				X	X	X	
Np				X	X	X	
For Beta/LEPS Analysis							
Tritium				X	EPA 906.0 ASTM D 2476	X	
C-14				X	X	X	
Ni-59,-63				X	X	X	
Se-79				X	X	X	
Sr-89,90				X	EPA 905.0	X	
Sr-90				X	X	X	
Nb-94,93m				X	X	X	
Tc-99				X	X	X	
I-129,-131				X	D2334	X	
Pb-210				X	X	X	
Ra-228				X	EPA 904.0	X	
Instrumental Analysis							
Gamma Spectroscopy				X	ASTM D 3649		
LEPS[9]					X		
Alpha Spectroscopy[9]					X		
Gross Beta Analysis[9]					X		
Gross Alpha Analysis[9]					X		
Beta Spectroscopy (LSC)9					X		

(a) See (7) in references for ASTM C numbers.
(b) Low Activity level sample.
(c) See (9) in references for EPA numbers. .
(d) See (6) in references for ASTM D numbers.

Notes:

1. New methods that produce less mixed hazardous waste are needed in all categories.
2. Soil sample collection from surface, sub-surface, and vadose zone for analytes listed.
3. Water sample collection from surface water and ground water for analytes listed.
4. Need microwave digestion methods for non-volatile isotopes.
5. Need sample prep method for volatile isotopes such as I-129, H-3.
6. Need sub-sampling protocols for high level soil samples.
7. Preparation of liquids, solids, and salts for various analytes listed.
8. Isolation of alpha emitters from high-level waste.
9. Instrumental analysis is considered to be independent of original sample matrix.

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METHOD DEVELOPMENT FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN MIXED WASTE

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ABSTRACT. While analytical methods exist for the determination of Resource Conservation and Recovery Act (RCRA) listed organic and inorganic compounds in hazardous materials, equivalent methods suitable for the characterization of radioactively contaminated samples are not at the same level of maturity. The Mixed Waste Methods Development Laboratory has been established at Los Alamos National Laboratory to address the need for such procedures. This presentation will focus on the efforts that have been directed toward the determination of volatile organic compounds (VOCs) in mixed waste matrices. The capabilities of the Mixed Waste Methods Development Laboratory will be outlined. Modifications to the containment boxes and analytical instrumentation required for the analyses will be described, as will experimental procedures and system performance benchmarks. Preliminary results from surrogate and real mixed waste matrices will be presented, and future directions for our method development effort will be discussed.

INTRODUCTION

Decisions concerning the handling, transportation, and disposal of mixed waste (combined radioactive and hazardous waste) are directly tied to characterization of the material in question. The U.S. Department of Energy (DOE), and more specifically DOE facilities that have been involved in nuclear activities, have generated a significant amount of radioactively contaminated hazardous waste that is in need of characterization. While analytical methods exist for the determination of Resource Conservation and Recovery Act (RCRA) listed organic and inorganic compounds in hazardous materials (1), equivalent methods suitable for the characterization of radioactively contaminated samples are not at the same level of maturity. Modified, or in some cases completely new, methods are required for mixed wastes due to the presence of radioactivity in the sample. A mixed waste characterization program has therefore been established at Los Alamos National Laboratory to address the need for such procedures. The majority of our work involving organic methods development is being conducted in the Mixed Waste Methods Development Laboratory (MWML). This lab is located in the Chemistry and Metallurgy Research building, a Category I Nuclear Facility at Los Alamos National Laboratory. A schematic layout of the laboratory is shown in Fig. 1.

Volatile organic compound (VOC) analysis is routinely performed on hazardous waste with a purge-and-trap apparatus to preconcentrate the sample, followed by gas chromatography/mass spectrometry (GC/MS). By installing the sample purge system in a containment box, we have been able to adapt this method (SW-846 Method 8260) (1) to mixed waste analysis.

While it will be necessary to deal with many different sample forms in the analysis of real wastes, it is desirable from a methods development standpoint to target certain representative matrices upon which analytical techniques can be based. We have chosen two waste forms for initial study:

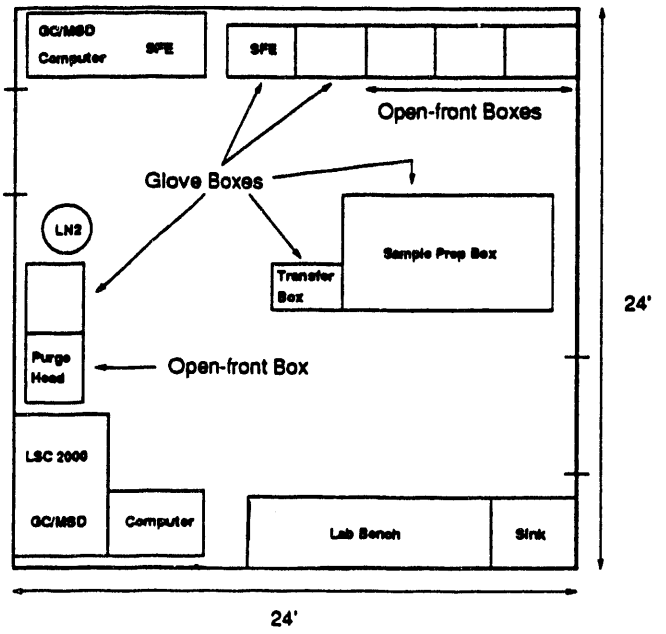

Figure 1. Schematic of Mixed Waste Methods Development Laboratory.

- Wastewater Treatment Sludge (stabilized and unstabilized)
- Ion Exchange Resins (stabilized and unstabilized)

Ultimately, our methods will be used to characterize TRUCON (TRanUranic CONtact handled) waste forms, examples of which include:

- TRUCON 111/211 (Wastewater Treatment Sludge)
- TRUCON 114/214 (Inorganic Process Solids)
- TRUCON 124/224 (Pyrochemical Salts)
- TRUCON 126/226 (Organic Process Solids)

The numbers are DOE designations for the different classes of waste, and the first digit signifies whether the material is "old" (1XX, produced before about 1985) or "new" (2XX).

In addition to the VOC method, we are developing techniques for semi-volatile organic compound (SVOC) analysis in the same laboratory. U.S. Environmental Protection Agency (EPA) SW-846 sample preparation methodologies for this class of compound involve extraction with organic solvents, and these techniques are not generally acceptable for use in a glovebox environment. Since SVOC analyses are so dependent on solvent extraction techniques, we have focused effort into the development of supercritical fluid extraction using carbon dioxide as the solvent. Since our proposed method has not been approved by the EPA, it will be necessary to prove equivalency between this method and existing SW-846 methods. To achieve this, some samples will need to be analyzed using both techniques, so we have also developed the capability to perform SW-846 SVOC sample preparation in a glovebox environment. While these methods are not covered in this paper, additional information on our work in this area is available (2).

Techniques that we develop are designed to be used for routine sample analyses at other DOE facilities, therefore we have attempted to employ widely available instrumentation wherever possible. In addition, the complexity of the equipment has been minimized to simplify both maintenance and operator training. In some cases, this approach has resulted in compromising the performance of the method. We are currently investigating instrumental modifications to alleviate this shortcoming. Minimizing both the sample size and handling requirements are also of the utmost importance in our methods, in order to keep worker radiation exposure As Low As Reasonably Achievable (ALARA), in accordance with both good laboratory practice and DOE directives (3).

EXPERIMENTAL

There are three containment box systems in the MWML (Fig. 1): a five-box train (3 open-front boxes and two gloveboxes), a two-box train (1 open-front and 1 glovebox), and a large glovebox equipped with 24 gloves and an additional side box for sample introduction and bagout operations. The five-box train is used for both general sample manipulations and for the supercritical fluid extraction system (used for SVOC sample preparation). Central Research Laboratories glove ports are used in this train, and allow glove changes to be performed in minutes with their sealed pass through enclosure system. The two-box train is used for the preparation/handling of VOC samples. Samples are introduced into the glovebox to be weighed and placed in solution. Once in solution, most samples can be safely transferred to, and handled in, the open-front box. The open-front box holds the purge head for the purge-and-trap apparatus (*vide infra*). The large box will be used for many different operations. Standard sonication and Soxhlet extraction equipment will be installed for verifying new SVOC methods against EPA SW-846 procedures. A total organic carbon/total inorganic carbon/total organic halide instrument is also scheduled to be installed. This apparatus will be used for screening analyses, and studies are underway to determine if the presence of organic solvent vapors in the box will affect the instrument background level. All of the boxes are coated on the inside with an electrostatically applied epoxy paint to improve corrosion resistance.

As mentioned previously, we are adapting EPA SW-846 Method 8260 for VOC analysis of mixed waste samples. Solid and semi-solid samples are prepared by first reducing the bulk solid samples to an appropriate particle size range by crushing and/or grinding the matrix. Subsequently water is added, a procedure commonly used on cold samples and apparently accepted by the EPA. Analysis then proceeds as stipulated by Method 8260. Aqueous samples may be purged directly. Samples in organic matrices (such as oils) are not easily analyzed by this technique, due to the high solubility of most analytes in the matrix. However, direct injection of these samples (with or without dilution) into the GC/MS may be possible with significantly reduced detection limits. This approach, however, has the disadvantage of requiring an injection port on the GC that prevents any activity from being introduced into the analytical instrument.

In keeping with our goals of simple and robust instrumentation, we have chosen a Tekmar LSC 2000 purge & trap system and a Hewlett-Packard GC/MSD (Model 5890 GC and Model 5971 Mass Selective Detector) for our methods development work. We have modified the LSC 2000 to allow placement of the purge head inside an open-front box (Fig. 2). We have also procured a 16-head purge system that can be used for preparing many samples at a time, followed by automated analysis. The adsorbent trap in the LSC 2000 is fitted with a thermoelectric cooler, to improve the recoveries for low-boiling point compounds.

In our modified method, ~ 1 g (0.001 kg) of the sample is placed into a 10 mL tube, 5 mL of water is added, and the tube is attached to the purge head. Helium gas is introduced via a needle sparger at a flow rate of ~ 25 mL/min for 12 minutes. This results in the effective transfer of the volatile components into an aerosol. The entrained analytes are then carried via a heated, 1/16" stainless steel transfer line to the adsorbent trap (Supelco VOCARB packing) where the organic analytes are deposited.

Due to the distance between the purge head and the trap (~ 1.5 m), the transfer line is heated to 180 °C (453

K) to avoid condensation of the volatile compounds on the inside of the line. Because actual samples may be radioactively contaminated, we must insure that any activity remains inside the containment box. Therefore, a particulate filter is installed in the transfer line connecting the purge system with the adsorbent trap. Several different filter types and combinations have been investigated. The selected configuration employs a commercially available 2 μm stainless steel screen (Nupro model SS-4FW-2) mounted at the bulkhead of the glovebox (Fig. 2). When highly contaminated samples are processed, and also at regular intervals during routine operations, this screen will be removed and counted. If the filter shows no activity, it can be assumed that no contamination has exited the box due to gas entrainment, and the analyses can safely continue. If activity is found, the assumption would be that the trap is contaminated, and the entire apparatus would be checked for contamination and cleaned if necessary. The 2 μm filters were chosen as a compromise between particulate restriction, back pressure generation, and analyte recovery considerations. Care must be taken to insure that both the transfer line and the particulate filter are effectively heated to preclude condensation of vapors within the filter because of the outstanding heat-sinking capabilities of the box wall at the bulkhead.

During the purge step, the adsorbent trap is held at 20 °C (298 K). Once the purge is completed, the trap is ballistically heated to 180 °C (453 K) and backflushed for 8 min at a flow rate of ~ 10 mL/min with He onto the head of the chromatographic column. After the desorption step, the trap is cleaned by baking for 10 min at 220 °C (493 K) and vented into the containment box in preparation for the next sample.

The GC separation column is a 30 m long, 0.25 mm i.d. fused silica capillary coated with a 2 μm film of methyl phenyl cyanopropyl silicone stationary phase (Quadrex Corporation, # 007-624-30-2.0F). This column has proven to furnish adequate separation for our target analytes (see Figure 3). The column is temperature programmed over the course of the analysis from 35 °C to 180 °C (303-453 K) at a rate of 7 °C/minute. The final temperature is held for 3 min. The chromatography is completed in about 24 min, resulting in a sample turnaround time of about 35 min. The mass selective detector is set up to scan from 35-350 amu (dalton) at a rate of ~ 1.7 scans/sec. We are currently using perfluorotributylamine as the mass spectrometer tuning compound. Tuning is automatically controlled by the data system, and is performed on a daily basis.

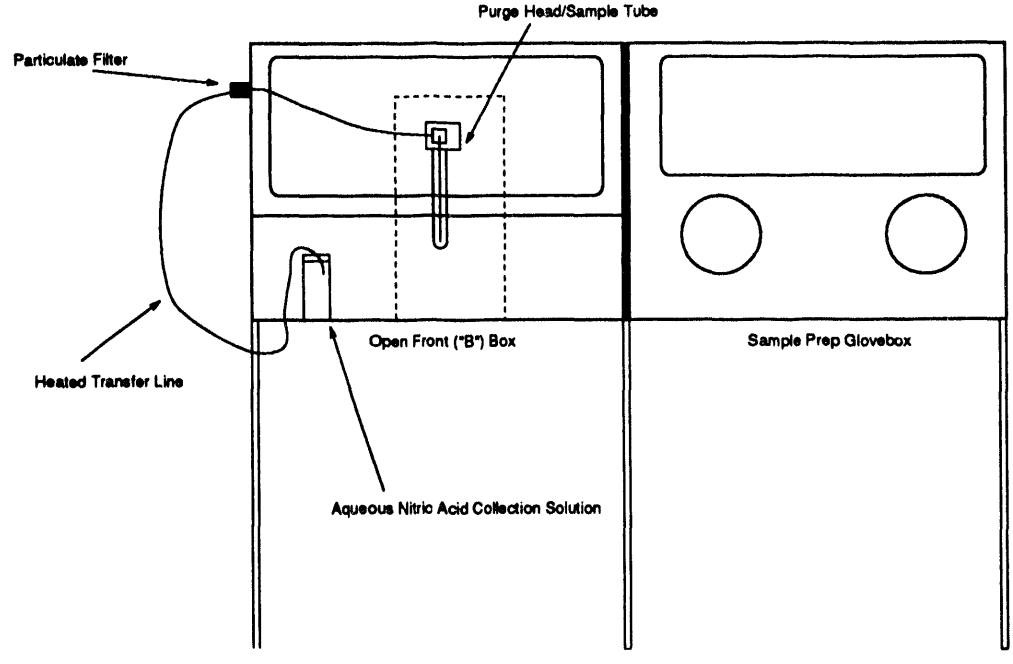

Figure 2. Schematic of the apparatus used in activity transfer experiments.

In order to measure the transfer of alpha activity from the purge tube, a slightly modified system is used. The heated transfer line that would normally carry the purge gas to the adsorbent trap is redirected back into the open front box and the gas is bubbled through a solution of dilute HNO_3, which will trap any entrained Pu alpha activity. A schematic representation of this configuration is given in Fig. 2.

RESULTS

After installation of the various experimental equipment, system performance was evaluated to determine optimal concentration and chromatographic conditions (flow rates, temperatures, etc.), and to benchmark the response of the instrument. A typical chromatogram, resulting from the analysis of a 50 ppm standard in reagent water, is shown in Fig. 3.

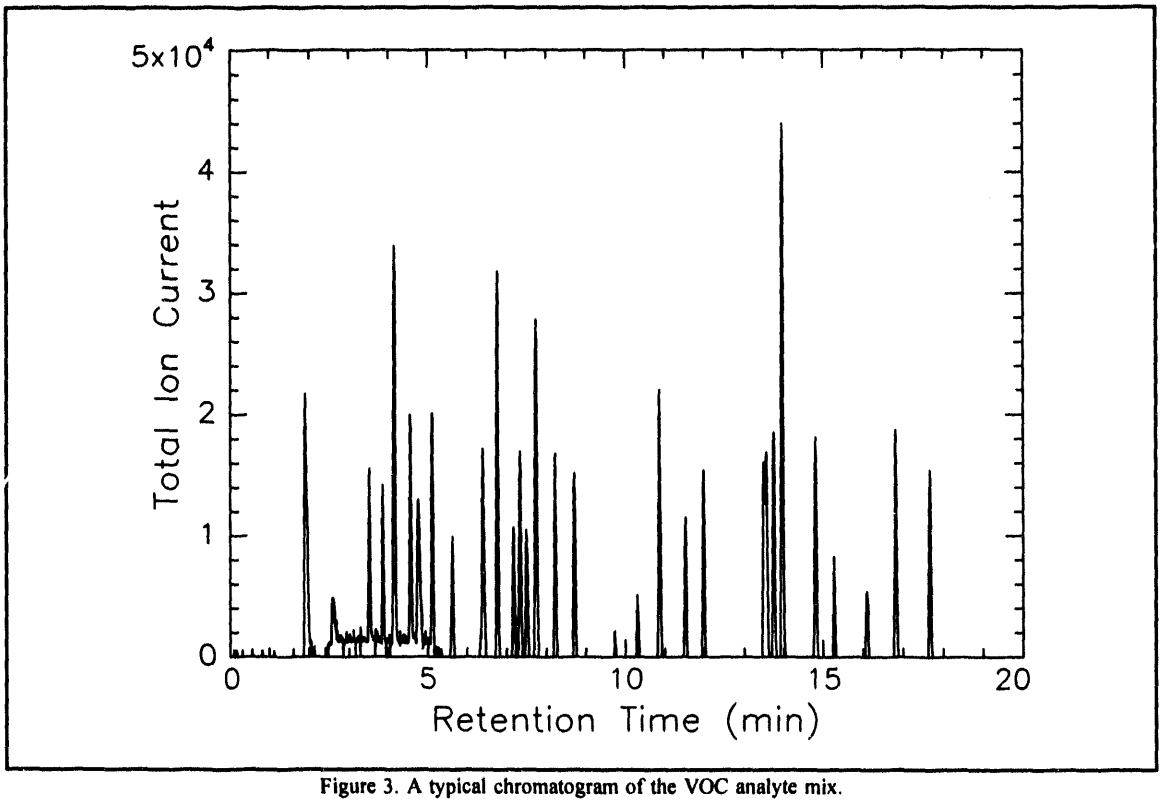

Figure 3. A typical chromatogram of the VOC analyte mix.

Method Detection Limits (MDLs) for the system were also determined (1). These values are listed for our analyte suite are presented in Table 1. After the final system configuration was set, a five-point calibration curve was constructed for our target compounds. System Performance Standards and Calibration Check Standards are regularly analyzed in accordance with Method 8260.

As can be seen, the values obtained with our method are generally on the order of a factor of 10 higher than those cited in Method 8260. The most likely reason for the discrepancy is our use of a small bore capillary column, which limits the amount of analyte that can be loaded onto the analytical instrument. It may be possible to increase the sensitivity of the current system by as much as a factor of 40 by using a wide bore (0.53 mm i.d.) capillary chromatographic column as opposed to the current 0.25 mm i.d. column, but the increased complexity of the interface between the GC and the MS (via a jet separator) may not be justified considering the performance of the current system, and the maintenance requirements and potential

Table 1. Method Detection Limits for selected VOC analytes.

Analyte	MDL (ppb) (this work)	MDL (ppb) (ref. 1)
vinyl chloride	1.54	0.17
trichlorofluoromethane	1.15	0.08
ethyl ether	0.84	N/A (not available)
1,1,2-trichloro-1,2,2-tri-fluoroethane	1.45	N/A
1,1-dichloroethene	1.80	0.12
acetone	4.75	N/A
carbon disulfide	1.20	N/A
methylene chloride	1.75	0.03
trans-1,2-dichloroethene	1.28	0.06
1,1-dichloroethane	0.88	0.04
methyl ethyl ketone	4.68	N/A
cis-1,2-dichloroethene		
ethyl acetate	2.16	N/A
chloroform	1.13	0.03
1,1,1-trichloroethane	5.46	0.08
cyclohexane	6.93	N/A
carbon tetrachloride	0.39	0.21
1,2-dichloroethane	3.15	0.06
benzene	3.10	0.04
trichloroethene	3.51	0.19
2-nitropropane	8.47	N/A
methyl isobutyl ketone	7.50	N/A
toluene	0.72	0.11
1,1,2-trichloroethane	2.82	0.10
chlorobenzene	0.29	0.04
ethylbenzene	0.51	0.06
m,p-xylene	0.55	0.13
o-xylene	0.88	0.11
bromoform	1.00	0.12
cyclohexanone	19.69	N/A
1,1,2,2-tetrachloroethane	1.40	0.04
1,3,5-trimethylbenzene	0.67	0.05
1,2,4-trimethylbenzene	0.71	0.13

operational problems associated with a jet separator. We are planning to evaluate this modification after we have completed our work with the present configuration.

In order to evaluate and quantitate the transfer of radioactive particles from the purge tube to the adsorbent trap, we have analyzed reagent water, surrogate wastewater treatment sludge (x), and several test samples using the experimental setup shown in Figure 2. The water and surrogate sludge were spiked with ^{239}Pu at levels ranging from ≈ 4.5 nCi/5 mL to 1 μCi/ 5 mL. After passing through the 2 μm particulate filter at the box wall, the transfer line is redirected into the glove box and bubbled through a solution of ~ 0.1 M HNO_3 to trap the Pu particles. This solution is subsequently analyzed for alpha activity by liquid scintillation counting. The filter is removed and sonicated in a clean HNO_3 solution, and subsequently analyzed using the same technique as the liquid. In all of our experiments, the results of which are summarized in Table 2, no radioactivity above background has been found on either the particulate filter or in the collected liquid. On the basis of these measurements, we do not believe activity transfer will be a problem with this method, however we plan to conduct further experiments to fully explore possible matrix-dependent activity transfer. For example, in matrices that foam significantly during the purge step (our surrogate sludge was one such waste form), there may be a larger propensity for radioactive material to be entrained in the aerosol and carried with the volatile analytes into the transfer line.

Table 2. Summary of activity transfer experiments.

Sample	Initial Activity Level (dpm/5 mL)	Transferred Activity Level (dpm/5 mL)
#1 - Reagent Water	10^5	< 50
2 μm Particulate filter from #1		< 50
#2 - Surrogate Sludge	10^5	< 50
2 μm Particulate Filter from #2		< 50
#3 - Reagent Water	2.2×10^6 (1 μCi)	< 17
2 μm Particulate Filter from #3		< 17

We have also determined the effect of the particulate filter on the recovery of sample components. As long as the filter body is effectively heated to the same temperature as the rest of the transfer line (453 K), no significant loss of the target analytes is observed. Recoveries with the filter in place are on the order of 70-95% for all of the compounds tested.

We have thus far analyzed four actual mixed waste samples for VOC contamination. Two of these samples were TRUCON waste materials (111/211 and 126/226) and the other two were a ^{235}U-contaminated ductwork sample. All were practically free of VOC content as measured by our method. The ductwork samples each contained ~ 15 ppb levels of methylene chloride. The total ion chromatograms for the TRUCON 111/211 and 126/226 samples are shown in Figs. 4 and 5, respectively. The significant peaks appearing in each data set are the matrix spike and internal standard compounds added to determine analyte recovery. The internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5, and the matrix spike compounds are compounds are 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. These species are all present at a concentration of 50 ppb in the samples.

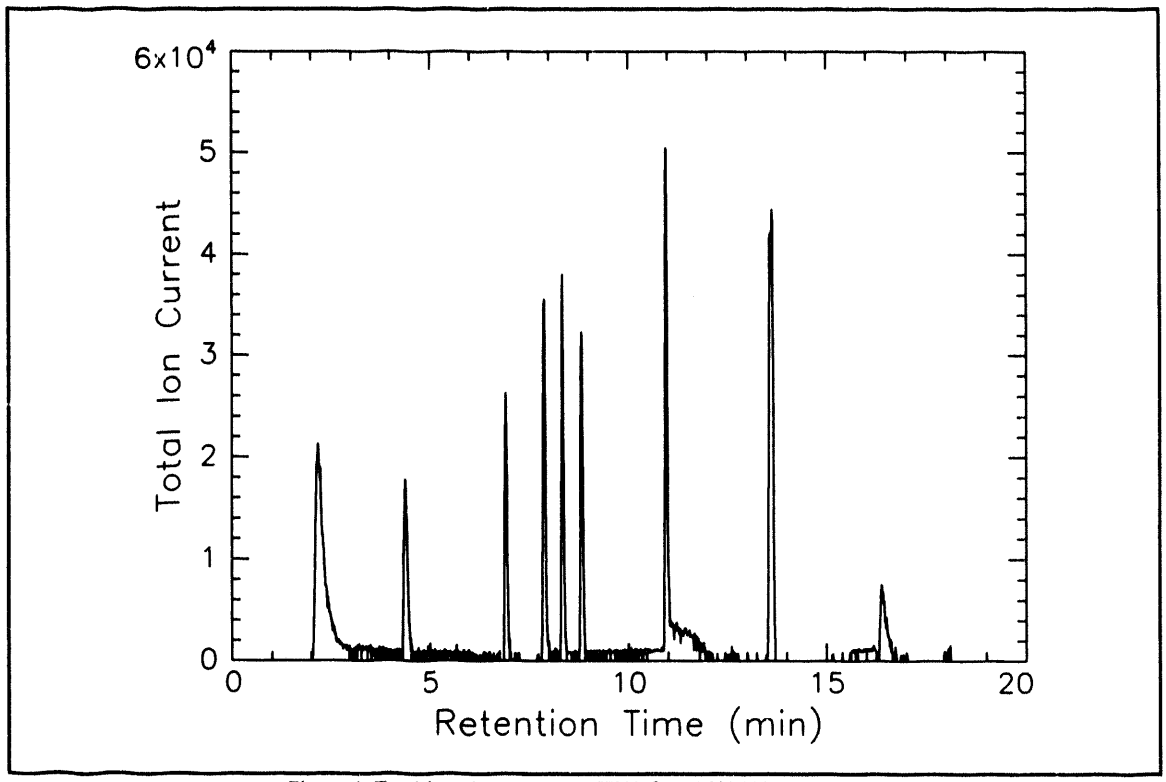

Figure 4. Total ion chromatogram (TIC) for TRUCON 211 sample.

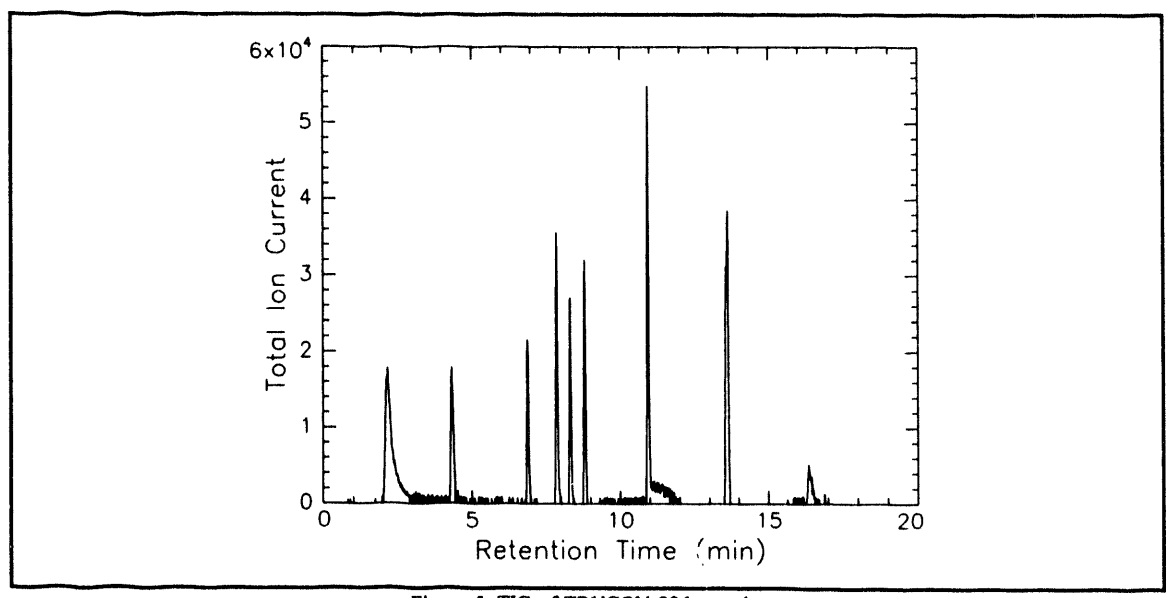

Figure 5. TIC of TRUCON 226 sample.

CONCLUSIONS

The MWML is a nearly complete facility capable of performing research on techniques for characterizing organic hazardous constituents in mixed waste matrices. We have presented here results of our preliminary VOC method for mixed waste matrices, which safeguards workers from unnecessary exposure to radiation hazards and allows the instrumentation to be maintained free of radioactive contamination from the analytical process. In addition to VOC analysis, the laboratory also has the equipment and personnel in place for semi-volatile organic compound (SVOC) and non-volatile (i.e. organic acids and ligands) analyses (2). These capabilities will be applied to characterize waste samples for certification for shipment to the Waste Isolation Pilot Plant. The analytical procedures we develop will be submitted to the DOE Analytical Methods Compendium for distribution to laboratories conducting mixed waste analyses.

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THE STANDARD LABORATORY MODULE APPROACH TO AUTOMATION OF THE CHEMICAL LABORATORY

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ABSTRACT. Automation of the technology and practice of environmental laboratory automation has not been as rapid or complete as one might expect. Confined to autosamplers and limited robotic systems, our ability to apply production concepts to environmental analytical analysis is not great. With the impending remediation of our hazardous waste sites in the United States, only the application of production chemistry techniques will even begin to provide those responsible with the necessary knowledge to accomplish the cleanup expeditiously and safely. Tightening regulatory requirements have already mandated staggering increases in sampling and characterization needs with the future only guaranteeing greater demands. The Contaminant Analysis Automation Program has been initiated by our government to address these current and future characterization by application of a new robotic paradigm for analytical chemistry. By using standardized modular instruments, named Standard Laboratory Modules, flexible automation systems can rapidly be configured to apply production techniques to our nations environmental problems at-site.

INTRODUCTION

As our government focuses on the need for remediation of its weapons complex sites, the anticipated sample analysis burden placed upon laboratories, both public and private, has become an issue of concern. Although the actual remediation has yet to really begin, projections of the numbers of samples required to promote an effective cleanup appear staggering. We feel that the introduction of integrated laboratory automation into our nations environmental sample analysis laboratories is the key. Standardized and modular laboratory automation promises to bring significantly higher accuracy, increased throughput, and enhanced worker safety to those responsible for this chemical characterization task. The Contaminant Analysis Automation program we will describe in this paper. Laboratory automation has traditionally been based on a robot intensive paradigm. In this paradigm, the robot is heavily relied upon to perform the sample preparation steps necessary before introduction to an analytical instrument. By relying heavily on the robot, the throughput gain from automation is all but lost. A much better paradigm for laboratory automation, based on the Standard Laboratory Module or SLM, is being developed by a interdisciplinary Department of Energy team within the Office of Technology Development. This paradigm is based on linking together chemical workstations which can autonomously perform sample preparation steps that are logically grouped as subtasks of an Environmental Protection Agency sample analysis method. Interaction with the robot is thereby minimized. This greatly improves the system throughput, its reliability, and component maintainability.

THE NEED FOR UNIQUE LABORATORY AUTOMATION

The Department of Energy (DOE) has significant amounts of radioactive and hazardous wastes stored, buried, and still being generated at many sites within the United States. These wastes must be characterized to determine the elemental, isotopic, and compound content before remediation can begin. We project that

sampling requirements will necessitate generating more than 10 million samples by 1995, which will far exceed the capabilities of our current manual chemical analysis laboratories. The Contaminant Analysis Automation effort (CAA), with Los Alamos National Laboratory (LANL) as the coordinating Laboratory, is designing and fabricating robotic systems that will standardize and automate both the hardware and the software of the most common environmental chemical methods. This will be accomplished by designing and producing several unique analysis systems called Standard Analysis Methods (SAM). Each SAM will automate a specific chemical method, including sample preparation, the analytical analysis, and the data interpretation, by using a building block known as the Standard Laboratory Module (SLM). This concept allows the chemist to assemble an automated environmental method using standardized SLMs easily and without the worry of hardware compatibility or the necessity of generating complicated control programs.

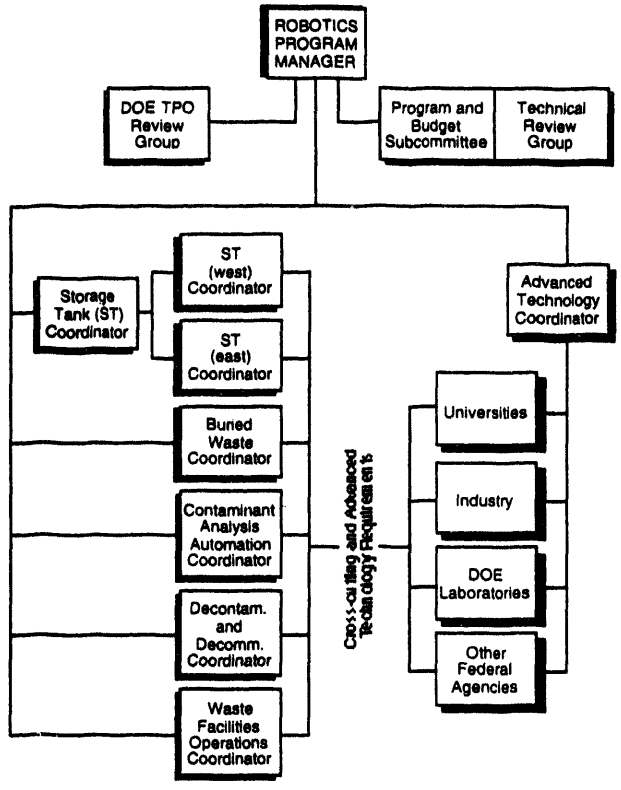

Figure 1. Robotics Program Organization

The Department of Energy's (DOE) Office of Environmental Restoration and Waste Management (ER & WM) has published and committed to a 5-Year Robotic Technology Development Program (RTDP) (1), aimed at assisting DOE hazardous material clean-up activities. The scope of the DOE robotic effort includes activities ranging from bench-scale Research and Development to full-scale hot demonstrations of technology. The program objectives were directed toward making clean-up activities at the national laboratories safer, faster, and cheaper. Outlined in Figure 1 is the Robotics Program organization. This highly collaborative effort encompasses ER & WM in areas such as above- and below-ground storage tanks (ST), buried waste, contaminant analysis automation, waste minimization, decontamination and decommissioning, and waste facilities operations. LANL is the lead laboratory in the CAA coordination area. The other laboratories involved in the CAA effort include Pacific Northwest Laboratory (PNL), Idaho National Engineering Laboratory (INEL), Sandia National Laboratories (SNL), Oak Ridge National Laboratory (ORNL), and Westinghouse Hanford Company (WHC). The CAA thrust is to address the development of technologies necessary for the automation of the DOE and DOE contract environmental

laboratories. This effort is in response to the tremendous need for chemical characterization of soil samples, contents of storage tanks, and water samples that must take place before remediation can be initiated.

To understand the magnitude of the required sampling, INEL estimates that the number of samples requiring analysis will increase from 28,000 to more than 55,000 by 1999, with approximately 65% being radioactive. The Hanford Site predicts that the number of low-level radioactive samples will increase from approximately 50,000 to more than 1,100,000 by the year 2003. Medium and high-level radioactive samples will increase from virtually zero to over 400,000. Without automating current environmental chemistry laboratories, the DOE will be unable to meet its needs for the remediation program. This scale of chemical analysis far exceeds current experience and will be the chemical equivalent of a production problem. Being very resource intensive, this effort is expensive (too expensive to accomplish manually). It demands more analysts than are available, and more facilities than currently exist. This effort is schedule driven by environmental laws such as the Resource Conservation and Recovery Act (RCRA) and Federal Facility compliance Agreements (FFCAs). The latter is a tri-party agreement between DOE, EPA, and the state where the DOE facility is located. FFCAs specify a timetable for site characterization and compliance with regulations.

THE CONTAMINANT ANALYSIS AUTOMATION PROGRAM

The CAA group came together in early 1990 to identify the priority analysis methods needing attention quickly, and to define the standards of modularity that would make the reconfiguration and operation of these automated systems intuitive. Two of the Environmental Protection Agencies (EPA) methods were identified for initial automation: EPA Method 3540 (the Soxhlet soil extraction) and EPA Method 3550 (the Sonication soil extraction).[2] Both of these methods are designed as organic analyte sample preparation methods. No automated commercial systems were available to automate these methods; the possibility of radioactivity being a further complication.

Initial discussions within the CAA team revealed that modularized and standardized chemistry (within both the software control and the hardware) were necessary if these automated systems were to be useful and transportable. The concept of on site sample analysis is shown in Figure 2. To provide valid data and timely sample analysis results, the team realized that it would be necessary to harden these systems so they could be transported directly to the remediation site. Another factor leading toward the modularity concept was the need for systems, which, leveraging standardization, could be configured by a knowledgeable chemist for a specific method and yet could be operated by a technician not versed in environmental chemistry.

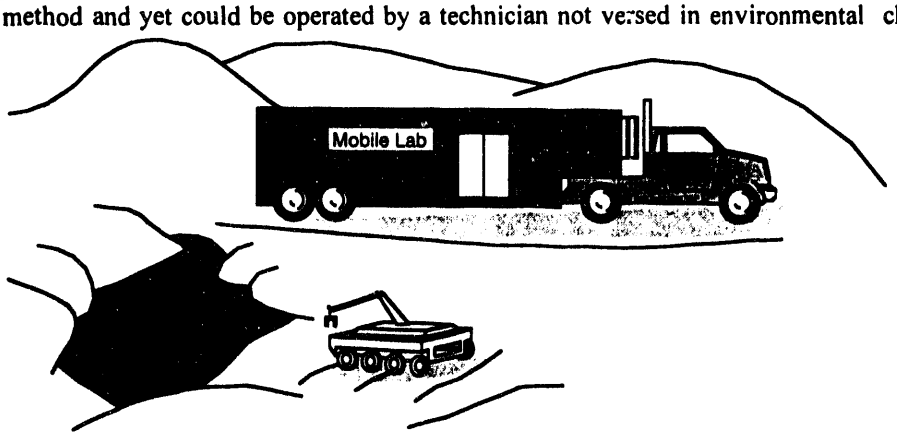

Figure 2. On-site Sample Analysis

The accomplishment of these goals required conceiving the Standard Analysis Method (SAM). The SAM is a glovebox-compatible grouping of subunits into a system that will accommodate current technologies. These subunits behave like modular building blocks. The SAM will accept samples from the field as input.

After automated sample preparation, the samples will be analyzed and the resulting raw data will be automatically interpreted by an expert system. The knowledge of the waste site generated by the SAM is then used for remediation. Each SAM includes a sophisticated, object-oriented database, within the system controller that tracks the sample in all phases of analysis, so that a detailed audit trail will be accessible for sample integrity and chain of custody verification. Making use of modular, open-architecture software allows the human-computer interface to be much more intuitive and allows the facile addition of new or different system capabilities. A graphical representation of the SAM concept is given in Figure 3. The SAM groups Standard Preparation Modules (SPM), an Analytical Instrumentation Module (AIM), and a Data Interpretation Module (DIM). One advantage of the modular SAM concept is its capability to accommodate emerging technologies. This capability results from the flexibility of the standardized hardware and software.

THE STANDARD LABORATORY MODULE

When the analysis method being executed by a SAM requires a sample preparation step, this function is subdivided within the SAM into a SPM, as shown in Fig 3. Many of the chemical methods that will be used for the remediation effort will require some sample conditioning or sample preparation. The EPA methods mentioned earlier are examples of sample preparation chemical procedures. SPMs are further subdivided into Standard Laboratory Modules (SLMs), which are the basic building-blocks of this automation scheme. In a SLM, the actual chemistry is performed and its internal functions are

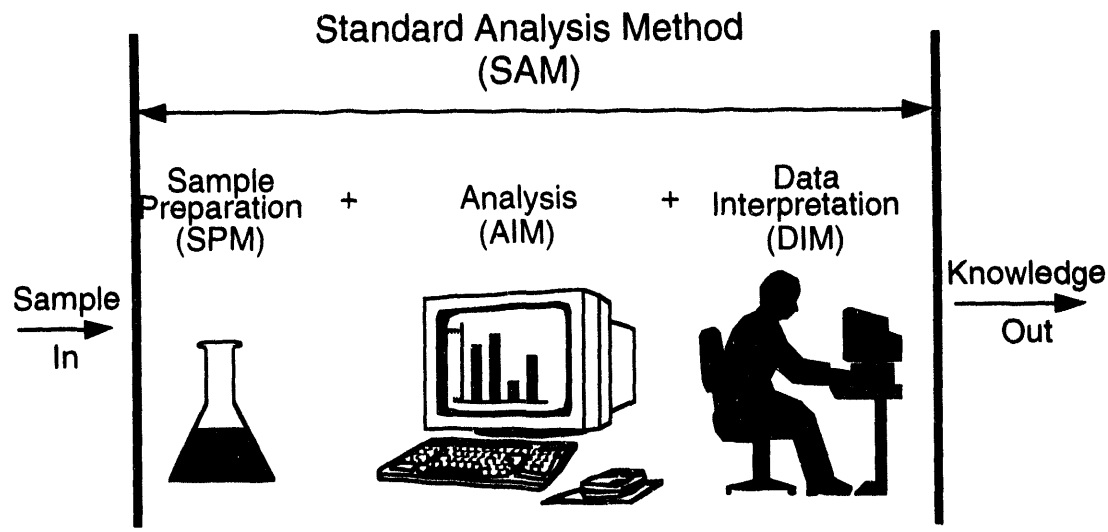

Figure 3. The Standard Analysis Method Concept

constrained by the method in question. For example, the Sonication SLM will accept a soil sample in a beaker, add reagents and standards, sonicate the sample, and vacuum transfer the extractant through an indexible filter into a clean beaker. When the SPM scheduler determines that the time is correct, this output beaker will then be taken from the Sonication SLM and input to the Drying Column SLM. The Drying Column SLM will then begin its operation. This philosophy of grouping logical tasks into hard-automated work-cells is a departure from traditional laboratory automation, in that, logical chemical manipulations are combined. Classical laboratory automation is operated on the paradigm of each manipulation being accessed

separately (that is, with solution dispensing separate from the sonication, which is separate from the filtration, etc.). This placed a heavy burden on the robot, and was not easily reconfigurable or adaptive. By combining logically similar functions in a SLM, robotic conveyance is minimized, and the system becomes efficient.

DEFINING THE SAM SYSTEM

A prepared sample generated by an SPM is then ready for the actual physical analysis that takes place in the AIM. This analysis is simply the characterization executed, for example, within a gas chromatograph, liquid chromatograph, atomic absorption spectrometer, or an inductively coupled plasma instrument. Many of these commercial instruments support autosamplers into which the SAM introduces the sample. These instruments will acquire the data which must then be interpreted. The DIM, existing as a software module within the SAM, uses knowledge-based algorithms in an expert system to generate characterization knowledge from the raw data of the AIM. The DIM can be configured to use a variety of pattern recognition algorithms and fuse the resulting analysis for verification.

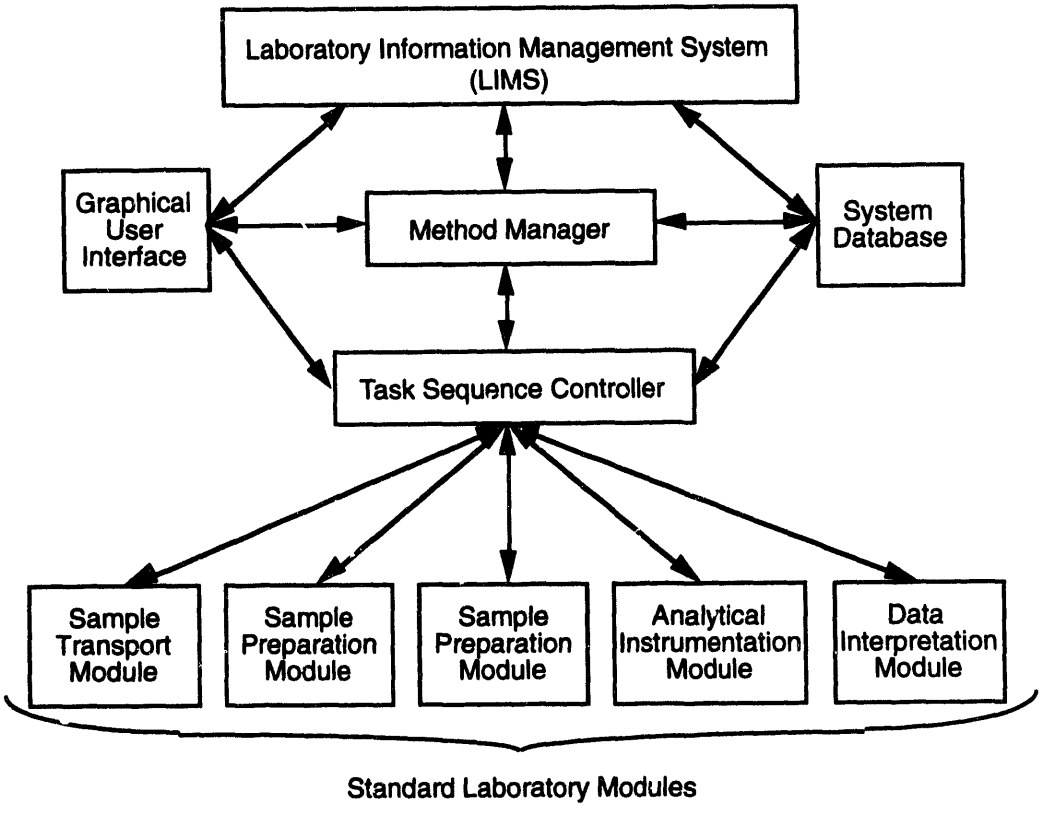

Figure 4. The Software Architecture

THE CONCEPT OF MODULAR CONTROL SOFTWARE

Known as the Automated Laboratory Control System (ALCS), this software follows the same modularity and standardization directives as the hardware. The operating system chosen was UNIX with SUNOS running on a SUN SPARC 2 workstation (host computer) and VxWorks, a real-time operating system, on the VME-bus processors. Using VME-bus based hardware, we are able to directly control stepper-motors,

analog and digital signals, and send or receive RS-232 messages. The control software is written in the C++ language. The SLM processors communicate with each other via a local VME bus and communicate with the host computer via an Ethernet connection. This multitasking environment allows the system to process multiple samples in an optimized fashion. The software architecture is shown in Fig 4. The automated laboratory interfaces with the site facility through its Laboratory Information Management System (LIMS). The Method Manager provides translation from high level chemical method definition to a lower level, hardware specific script of commands necessary for SLM execution of the method. The Task Sequence Controller (TSC) performs script processing and supervisory control of the SLMs in the system. The System Database serves as the information store for the automated laboratory. System administrative information, sample tracking, raw results, processed results, and reports are all stored in the database. The Graphical User Interface provides operator access to the LIMS, Method Manager, Database, and Task Sequence Controller. Each SLM has it's own intelligent controller for performing real-time control of the chemical workstation.

Method Manager, System Database, Graphical User Interface, and Task Sequence Controller all reside on the UNIX workstation. The SLM controllers reside on CPUs in the VME-bus CPUs. The communication link between the UNIX workstation and the VME-bus system is ethernet.

STATUS OF THE CAA PROJECT

When EPA methods 3550 and 3540 were chosen as the targets for our initial automation SLM design and construction, responsibility was divided up roughly as shown in Fig 5. The SLMs for the Soxhlet procedure

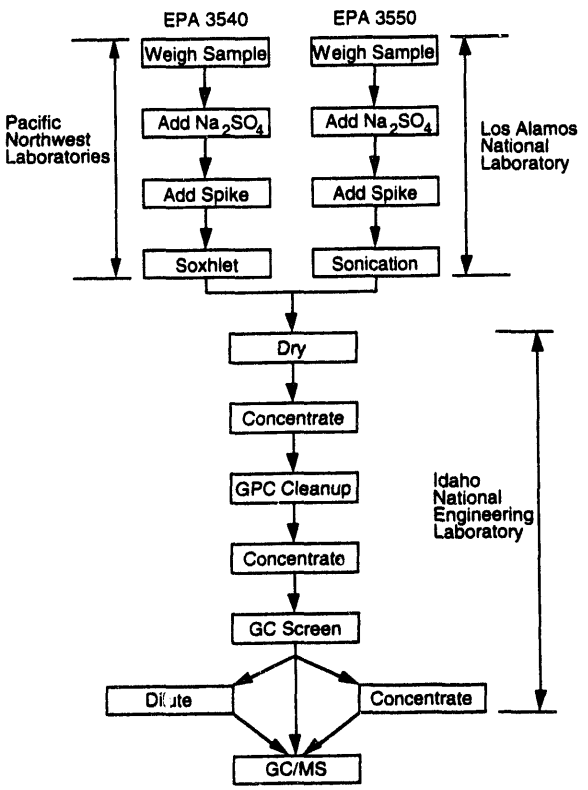

Figure 5. CAA program responsibility.

were developed by PNL, and the SLMs for the Sonication procedure were developed by LANL. The common SLMs, shared between these methods are being engineered by INEL, who has completed the Drying-Column SLM and the GPC SLM. These units were conceptually demonstrated as an enclosed integrated system in March 1992 at the INEL, as shown in Fig 6. Two Hewlett Packard (HP) ORCA[tm] rail-mounted robots were used to move samples between the SLMs and an HP gas chromatograph to demonstrate the concept of the automated environmental analysis laboratory. The benchtop is a rectangular geometry and can be located inside existing laboratories. A hooded enclosure contains the system, providing ventilation for the solvents used. Pre-weighed samples enter the system in glass beakers, and are shuttled from SLM to SLM by the robots. When a sample has completed the sample preparation steps from extraction through gel-permeation chromatography cleanup, it is placed in autosampler queue of the gas chromatograph for analysis.

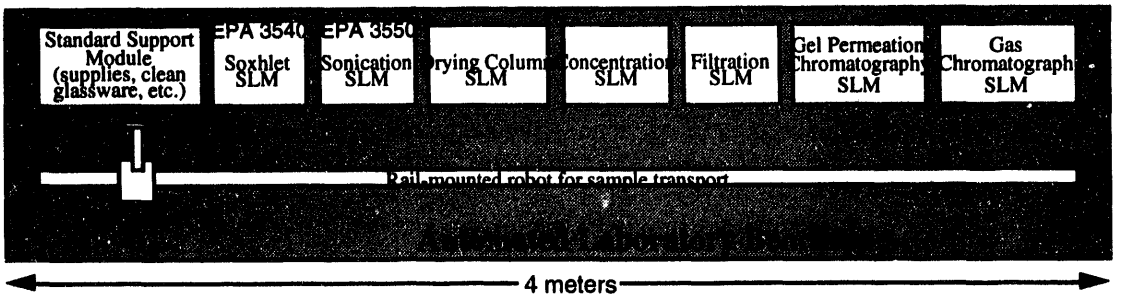

Figure 6. Demonstration setup.

Since this demonstration the Concentration SLM , the Filtration SLM, and the Fluid Transfer SLM have been designed and are being laboratory tested. The initial SLMs are ready to be EPA validated as not deviating from the SW 846 methods compendium and the three latest SLMs will be validated subsequently. A fully functioning SAM for EPA's Methods 3550 and 3540 is scheduled to be in place, ready for EPA method validation by late 1993 (2). We have also made significant progress in the area of transferring this technology into the private sector. The need for a Systems Integrator to support our development efforts became obvious to our team. This industry partner will be responsible for finding potential customers, accessing their needs, and for configuring and supporting SAMs Systems to meet these customer needs. A team composed of Lockheed collaborating with Hewlett-Packard was selected as our Systems Integrator. We are currently working together to identify other industrial partners who might help develop and manufacture specific Standard Laboratory Modules.

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ENVIRONMENTAL MONITORING: AN AIDE TO MIXED WASTE MANAGEMENT

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ABSTRACT. The U.S. Department of Energy's Hanford Site was established in southwestern Washington during the early 1940s to produce plutonium for the war effort. Environmental monitoring has been an ongoing activity for almost 50 years. Monitoring objectives are to detect and assess potential impacts of Site operations on air, surface and ground waters, foodstuffs, fish, wildlife, soils and vegetation. Data from monitoring efforts are used to calculate the overall radiological dose to people working onsite or residing in nearby communities. Monitoring for chemicals is now receiving increased attention. In addition to monitoring radioactivity and chemicals in fish and wildlife, population numbers of key biotic species are determined.

Currently, measured Hanford Site perimeter concentrations of airborne radionuclides are below applicable guidelines. Concentrations of radionuclides and nonradiological water quality in the Columbia River are in compliance with applicable standards. Foodstuffs irrigated with river water downstream of the Site show levels of radionuchdes that are similar to those found in foodstuffs from control areas. Low levels of ^{137}Cs and ^{90}Sr in some onsite wildlife samples and concentrations of radionuchdes in soils and vegetation from onsite and offsite locations are typical of those attributable to worldwide fallout. The calculated dose potentially received by a maximally exposed individual (i.e., based on hypothetical, worst-case assumptions for all routes of exposure) in 1991 (0.02 mrem/yr) was similar to those calculated for 1985-1990.

Chinook salmon (Oncorhynchus tshawytscha) continue to spawn in the Hanford Reach of the Columbia River and attract bald eagles (Haliaeetus leucocephalus). An elk (Cervus elephus) herd, established by imgration in 1972, is increasing. The Hanford Site also serves as a refuge for Canada goose (Branta canadensis), great blue heron (Ardea herodias), and various plants and other animals, e.g., mule deer (Odocoileus hemionus) and coyote latrans).

Although the Site's mission has changed from nuclear materials production to environmental cleanup, monitoring remains no less important. Certain cleanup actions may, ironically, increase rather than decrease exposures, first to workers and second to the offsite public as contaminants are exposed or released to various enviromental media. This paper reviews the historical monitoring program at Hanford and the changes anticipated to keep pace with cleanup activities that reflect the site's new mission.

INTRODUCTION

The U.S. Department of Energy's (DOE) Hanford Site occupies a land area of about 1,450 km^2 (560 mi^2) in semi-arid southeastem Washington, U.S. A. (Figure 1). Since 1943, the most environmentally significant activities have involved the production of nuclear materials, and associated chemical processing and waste management. Byproduct wastes have included gamma, beta, and alpha-emitting radionuclides and non-radioactive chemicals in gaseous, liquid and solid forms.

There are four major operations areas on the Hanford Site (Fig. 1). The 100 Areas located along the Columbia River include the reactors (now deactivated) that produced plutonium for national defense and the Hanford Generating Project (HGP). The 200 Areas contain reactor fuel reprocessing and waste-disposal facilities. The 300 Area, located north of Richland, Washington contains the uranium fuel manufacturing facilities and several research and development laboratories. The 400 Area includes the Fast Flux Test Facility which has operated intermittently to test new fuels and materials for future breeder reactors. Non govemment facilities include HGP, three commercial power plant sites, and a commercial low-level radioactive waste burial site near the 200 Areas.

Environmental monitoring has been conducted at Hanford for almost 50 years to assess potential impacts from exposure to radionuelides, ionizing radiation and hazardous chemicals. Media sampled include air, surface and ground waters, foodstuffs (fruits, vegetables, milk, etc.), fish, wildlife, soils and vegetation. Emphasis on chemical monitoring has increased over the last several years. Fish and wildlife are also monitored to determine population status of key species.

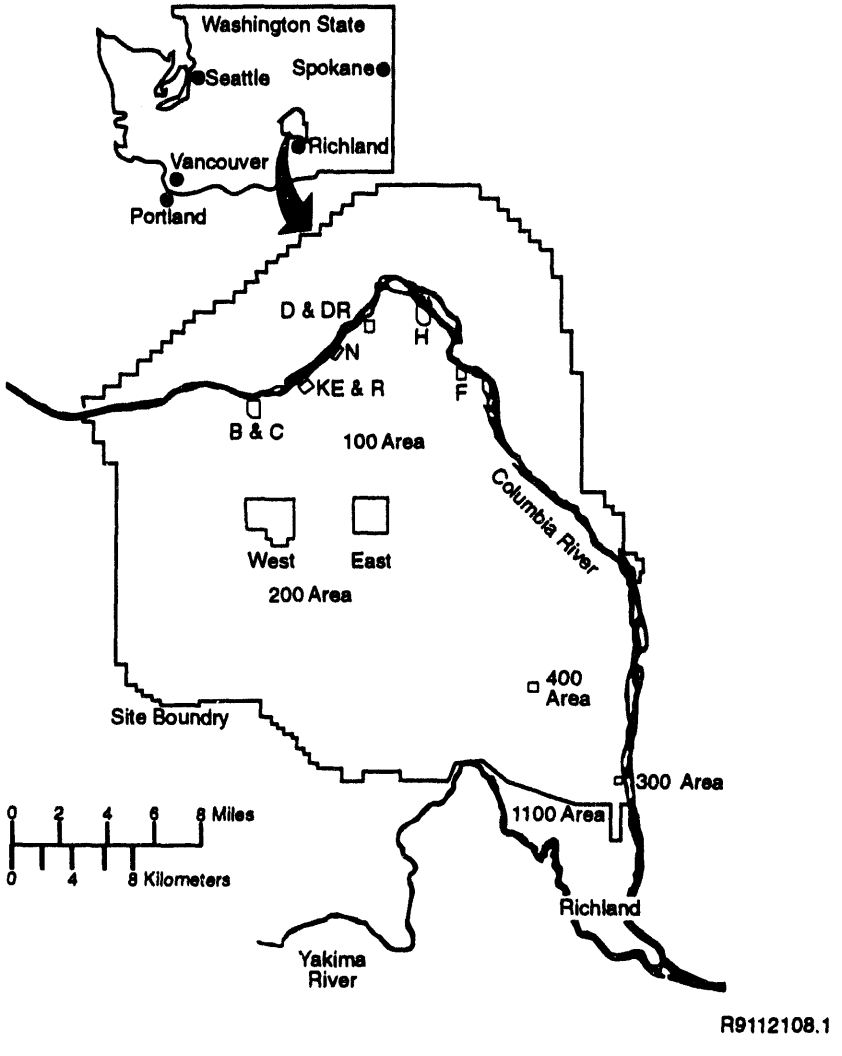

Figure 1. The Hanford Site, Southeastern Washington. B, C, KW, KE, D, DR, N, H, F = production reactors.

RADIOLOGICAL MONITORING

Air

Air is sampled continuously for airborne particulates and analyzed for radionuclides at 50 onsite and offsite locations (1). At selected locations, gases and vapors are also collected and analyzed. In May and June, 1986, air samples showed increases in several long- and short-lived radionuclides (e.g., ^{137}Cs, ^{131}I, ^{103}Ru) that resulted from the reactor accident at Chemobyl. Even then, no sample exceeded 0. 17 % of the applicable DOE derived concentration guide (DCG) for areas permanently occupied by the public.

Surface Water

Columbia River water is used for drinking, crop irrigation and recreational activities. Radionuclide concentrations in the Columbia River are below federal and state Drinking Water Standards (DWS).

Ground water

Ground water is sampled from over 450 wells and analyzed for radionuclides (1). Tritium (^{3}H), one of the most mobile radionuclides, reflects the extent of ground-water contamination from onsite operations. Tritium concentrations in Hanford ground water range from less than 300 pCi/L to over 2 μCi/L near or within the 200 Areas. Ground water from the unconfined aquifer enters the river through springs that emanate from the riverbank (2). From 1983-1989, annual average ^{3}H concentrations in the river (< 200 pCi/L) were at least a factor of 100 below the drinking water limit (3-6).

Foodstuffs

Foodstuffs, including milk, vegetables, fruit, beef, chickens, eggs and wheat, are collected from several locations, primarily downwind of the Site (1,3-6). Radionuclide concentrations ^{90}Sr, ^{129}I, and ^{137}Cs) in samples collected near Hanford are similar to those in samples collected away from the Site.

Fish and Wildlife

Fish are collected at various locations along the Columbia River and analyzed for ^{60}Co, ^{90}Sr, and ^{117}Cs. Radionuclide concentrations in fish collected from the Hanford Reach of the Columbia River are similar to those in fish from upstream locations (1,3-6).

Deer, pheasants, ducks, and rabbits are collected and tissues are analyzed for ^{60}Co and ^{137}Cs (muscle), $^{239,240}Pu$ (liver) and ^{90}Sr (bone). Doses that could be received by consuming wildlife at the maximum radionuclide concentrations measured in 1985-1991 were below applicable DOE standards (1,3-6).

Soils and Vegetation

Surface soil and vegetation are collected at 52 locations (1). Sampling and analyses in 1985 through 1991 showed no radionuelide buildup offsite that could be attributed to Hanford operations (1,3-6).

Overall Radiological Impact

Using worst-case assumptions for all routes of exposure, a hypothetical maximally exposed individual received 0.02 to 0.1 mrem annually from 1985 through 1991 (1,3-6). The average per capita effective dose based on the population of 340,000 to 380,000 people living within 80 km (50 mi) of the Site, was <0.01 to 0.03 mrem annually. Radiation doses to the public from Hanford operations have been consistently below applicable standards, and substantially less than doses from other routinely encountered sources of radiation (Fig. 2).

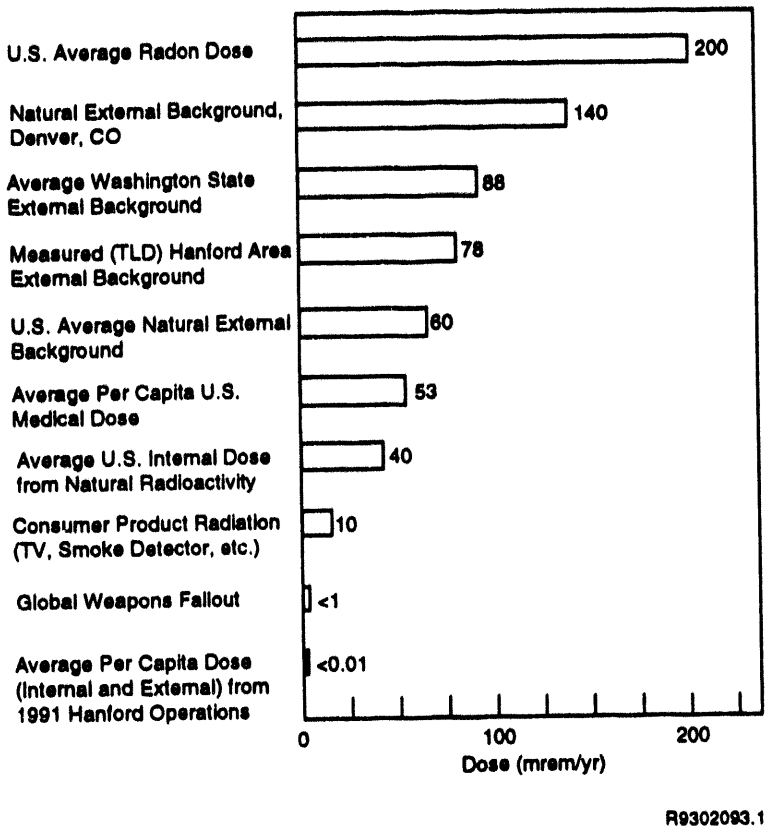

Figure 2. Annual radiation doses from various sources [see refs. 1,3-91. TLD = thermoluminescent dosimeter, does not include neutron component; mrem/yr = millirem per year.

CHEMICAL MONITORING

Air Quality

Nitrogen dioxide was sampled until PUREX ceased operations in 1990; concentrations measured in 1984-1990 were well below federal and state ambient air quality standards (1,3-6, 10).

Columbia River

Nonradioactive waste water discharges to the Columbia River are monitored under a National Pollutant Discharge Elimination System Permit. The Columbia River is also monitored by the United States Geological Survey (USGS), upstream and downstream of the Site, to verify compliance with state (11) water-quality requirements. The Columbia River at Hanford is designated Class A, Excellent. Thus, it is usable for all needs including drinking water, recreation and wildlife.

Recently, Columbia River water was sampled in transects both up- and downstream of the Site (12). The samples were analyzed for volatile organic compounds (VOCs), metals and anions based on the known presence of these constituents in ground water near the river and studies documenting their entry into the river. VOCs were not routinely detected. Several metals and some anions were detected at levels comparable to those reported by the USGS (13). There were no measurable differences between up- and downstream concentrations of metals and anions in river water.

Ground Water

Ground water, including onsite drinking water sources (not public), is collected and analyzed. Detected constituents included several metals, anions, coliform bacteria, radionuclides and total organic carbon. Chromium, cyanide, fluoride and carbon tetrachloride are found in wells not used for drinking near operating areas.

HANFORD FLORA AND FAUNA

Most of the Site consists of undeveloped land that has been essentially free from agriculture, livestock grazing and hunting for 50 years. Restricted land use has favored native wildlife that frequent riverine habitats, e.g., mule deer, Canada goose, and great blue heron. The Site also serves as a refuge for other migratory waterfowl, elk, coyote, and a variety of other plants and animals (14).

The Columbia River at Hanford supports up to 48 species of fish (15) and serves as a migration route for chinook, coho and sockeye salmon, and steelhead trout, and supports the last remaining mainstem spawning habitat for fall chinook salmon. Steelhead trout also spawn in the Hanford Reach. Fall chinook salmon spawning at Hanford Reach increased dramatically from 1980 through 1989 (Fig. 3a) with a concomitant increase in the number of wintering bald eagles (Fig. 3b).

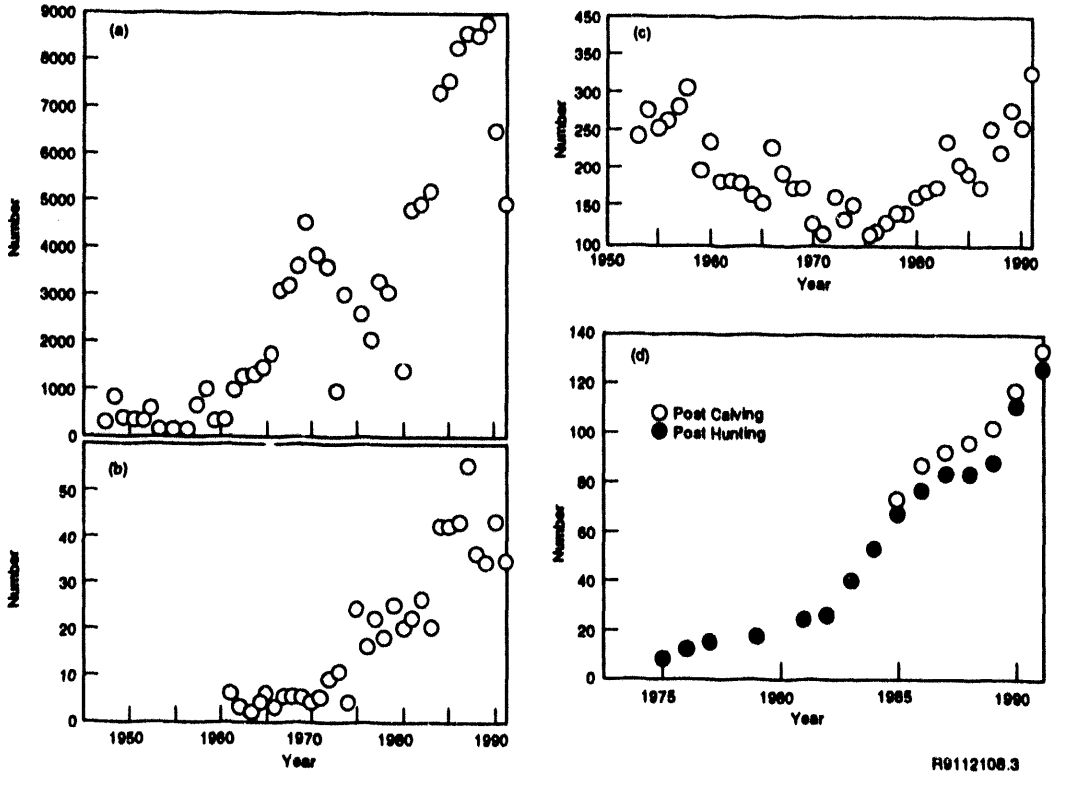

Figure 3. Numbers of (a) Chinook Salmon Redds (Nests), (b) Wintering Bald Eagles, (c) Canada Goose Nests, and (d) Elk at Hanford (1,14,16). Special permit hunting offsite for elk began in 1986.

From the mid-1950s to the mid-1970s the number of goose nests on the Hanford Reach declined from 250-300 to about 100 annually. From the late 1970s to the present, the number of nests has increased to over 300 (Fig. 3c). Although there were originally no nesting great blue heron on the Hanford Site, there are now four active colonies consisting of about 35-40 or more birds each (14).

Elk first arrived on the Hanford Site in 1972. The herd size now exceeds over 135 animals (Figure 3d). The mule deer population at Hanford is estimated at several hundred animals.

ENVIRONMENTAL CLEANUP

The mission of the Hanford Site has recently changed from nuclear materials production to environmental cleanup and restoration. Areas targeted for cleanup contain mixtures of radionuclides, chemicals or both. Numerous challenges face those involved with developing a coordinated and consistent approach to this new mission. Ironically, many cleanup options have the potential to increase rather than decrease exposures first, directly to workers involved in the cleanup process and, second, indirectly to the public and environment as buried or contaminated waste is temporarily exposed to the elements (17). While cleanup may reduce the volume of highly contaminated material, the volume of material with low-level contamination (filters, piping, clothing, etc.) will increase. Materials that become contaminated during the cleanup process will have to be treated, buried in situ, or transported and re-buried elsewhere. If old or newly contaminated material must be treated or re-buried at some distant location, the risks of transportation must also be considered. In situ cleanup options such as vitrification (solidifying or glassifying through use of an electric current) and grouting (transformation to cement) could be the preferred treatment methods, although much additional study of these fledgling technologies is needed.

Regardless of which cleanup options are chosen or the level of cleanup to be attained, environmental monitoring will continue as an aide to waste management during the 30 plus year cleanup process and for decades beyond. Monitoring is required to assure worker, public and environmental safety. Current modifications to the program call for increased emphasis on monitoring for hazardous chemicals and on monitoring those areas where the public can come in contact with the Site. These include the Columbia River, its shoreline and islands.

ACKNOWLEDGMENTS - Sitewide environmental monitoring has been conducted by PNL since 1965, and is supported by DOE under Contract DE-AC06-76RLO 1830 with Battelle Memorial Institute.

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SELECTING A RADIOANALYTICAL LABORATORY

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ABSTRACT. With the concern for cleanup of radioactive and mixed waste sites mounting, fast and accurate analyses of radionuclides in environmental matrices is of vital importance. Due to the increased demand for such analyses, many radioanalytical laboratories have recently been constructed. Since the analyses for environmental radioactivity are relatively new to the analytical services industry, the task of evaluation of such prospective laboratories by a firm seeking radioanalytical work is often a difficult one, due to a lack of specific knowledge regarding such areas as radiation licenses, radiochemistry methodology, proper quality assurance and reasonable turn-around times. Lacking a clear-cut understanding of this specialized type of analyses, such clients find themselves too frequently at the mercy of the service laboratory. What are the criteria for choosing a radioanalytical laboratory? Discussed in detail in this paper are the key ingredients for such a selection process, under the headings of qualified personnel, quality assurance program, methods of analysis, laboratory facilities, radiation license and client services.

QUALIFIED PERSONNEL

The shortcomings of many radioanalytical laboratories can be traced to the absence of qualified personnel. The fact is that experienced, cognizant radiological personnel are difficult to find. This situation exists primarily because there are few academic training programs at the university level for this area of expertise. Radiochemistry, for example, is somewhat of an unwanted stepchild, fitting neither into the chemistry nor the nuclear engineering curricula. Consequently, virtually all radiological training is presently being acquired through on-the-job experience at nuclear power plants, national laboratories, etc.

Companies attempting to plan for and implement the start-up of a radiological laboratory without such key, technically qualified personnel inevitably sow seeds for serious quality problems down the road, leading to poor audit evaluations, unacceptable performance on cross check and blind analyses and serious breaches with clients due to inaccurate data, incorrect data interpretation, poor quality control analyses, etc. The technical leadership of qualified radiological personnel is, uncompromisingly, a must.

Specifically, there are three areas of radiological expertise which are essential to the favorable operation of a radioanalytical service laboratory. The first is that of radioactivity counting theory and practical aspects of detection. This includes a deep working knowledge of gamma spectroscopy, alpha spectroscopy, liquid scintillation counting and gas proportional counting.

Common to all of these areas of counting expertise is the necessity for a firm grasp of the theory and hardware of the pertinent detection system, energy and efficiency calibrations, detector background, counting geometries, statistics of counting and necessary QC checks. All of these are of key importance in the proper day-to-day operation of the instrumentation. In addition, it should be pointed out that the computer software programs for such counting and subsequent calculations, though menu-driven, frequently require the attention of one who is intimately familiar with the system programming and operation. Thus, each radiological counting lab should have a system expert.

The qualified gamma spectroscopist should, be highly skilled in the interpretation of gamma spectra, giving careful attention to the radionuclide peak energies and resolution. The experienced spectroscopist must be able to take into account the gammas anticipated from a given sampling site (e.g., what would be expected from the vicinity of a nuclear power plant versus a uranium tailings site) in making the qualitative assessment of what gamma-emitting radionuclides are present in an analyzed sample. Where two or more radionuclides having the same or nearly the same gamma energy are eligible candidates for being assigned as detected in a sample, the technical expert should know which of these is the correct selection, and whether or not this can be verified by the presence of other, less abundant peaks.

Expertise with alpha spectrometry is also an absolute requirement. The alpha spectroscopist must exercise sound judgement in evaluating the resolution of the spectral peaks, since the degradation of spectra due to self absorption can significantly alter the analysis results. A knowledgeable analyst will be able to discern extraneous activity in the spectra, and will be cognizant of potential sources of recoil contamination of detectors. A comprehensive understanding of radionuclide peak energies, together with the ability to recognize the presence of contaminant nuclides, is imperative.

The radioactivity counting expert should be well versed in the theory and operation of liquid scintillation counters. Such areas as quench correction, window settings, background subtraction, appropriate counting times, dark adapting, cpm/dpm and low-level counting modes and alpha/beta discrimination should be readily understood. The proficient specialist will be able to detect counting aberrancies and spectral contamination.

The fourth area of necessary expertise in radioactivity counting is that of gas proportional counting. Comprehensive knowledge of high voltage plateau determination and interpretation, proper gas flow and instrument software for operation and calculations is necessary. Recognition of poor instrument performance, resulting in spurious counts, drastic changes in detector efficiency and excessive backgrounds, is critical.

Supplementing the specialist knowledge in counting is the expertise required in radiochemistry. In addition to the basic skills of the laboratory chemist, extensive familiarity with radiochemical operations, not part of the domain of conventional analytical chemistry, is an absolute requirement. These include such radiochemical separation approaches as ion-exchange, co-precipitation, solvent extraction, radon de-emanation and electrodeposition. These techniques are often tricky, complicated and fraught with potentially serious difficulties and obstacles. It should be noted that for the radioanalytical service laboratory offering an all-inclusive range of analyses, a broad, yet detailed understanding of many different radionuclide separation methods is required of the radiochemistry expert. This point will be covered in more depth in the section below on methods of analysis. Additional expertise is needed in the handling of a wide variety of matrices for preparation and analyses, and the proper use of radiotracers for yield monitoring.

The third critical area of technical expertise required for the proper functioning of a radioanalytical laboratory is radiation licensing/health physics. It is necessary to engage a knowledgeable person in this area in the early phases of lab start-up. This expert must be able to deal with all aspects of radiation licensing issues, including appropriate activity levels, radionuclides to be covered in the license, radiation detection equipment, personnel monitoring, swipe tests, sample screening, radioactivity source inventory, radioactive waste disposal and radiation safety training. It is imperative that this individual, who would function as the laboratory's Radiation Safety Officer have the proper background and experience so as to engender the implicit trust and confidence of the licensing body.

One important observation is that most often, the three primary areas of expertise essential to the success of the radiological service laboratory, radioactivity counting, radiochemistry and radiation licensing/health physics, are most often acquired through the engaging of more than one specialist, since it is only infrequently that all of these key skills are found in one expert. Once these qualified personnel are retained, however, they can effectively train other non-radiologically trained workers who do have analytical chemistry experience. This training should be rigorous and well-documented (see section below on Quality Assurance Plan or QAP).

In summary, the acquisition of radiological technical experts is imperative for the successful operation of a radioanalytical service laboratory. The failure to address the critical need for this expertise, even in the early stages of laboratory start-up, will lead to serious quality problems.

QUALITY ASSURANCE

Presently, there are many sources of guidelines for the development of a radiological laboratory's Quality Assurance (QA) program. Since there are no U.S. Environmental Protection Agency (EPA) or U.S. Department of Energy (DOE) standard QA protocols for radioanalytical analyses, the QA requirements that are in current use are adapted primarily from EPA SW-846 (1), EPA-600/4-80-032 (2), quality assurance program requirements for Nuclear facilities (NQA-1) (3), and HASL-300 (4) documents. These references are designed for drinking water (EPA), DOE research analyses (HASL-300) and nuclear power plants (NQA-1), none of which adequately addresses the requirements of a QA program for full service radiological laboratories. Lacking clear direction, individual laboratories are left to develop QA guidelines on their own which are an appropriate blend of all of the above criteria.

The cornerstone of any laboratory's QA program is their QAP. Since most radioanalytical laboratories are required to conform to regulations that apply to drinking water, waste water, DOE waste sites, mill tailings, etc., the QAP must be broad in scope.

The QAP must first define the role of the QA management. The key to any good QA program is to ensure that the QA management is independent of the production management, and that the QA management has the authority to halt production if any quality issues are in question. Also under the purview of QA management are such items as document control, communications, internal QC checks, internal audits, Performance Evaluation programs, Method Detection Limit verification and Good Laboratory Practices. For the radiological laboratory, participation in EPA's Environmental Monitoring Systems Laboratory - Las Vegas and the DOE's Environmental Measurements Laboratory cross check programs is a good check of the laboratory's ongoing performance and is frequently required by auditors.

One constituent of the QAP that is becoming more of a rigid requirement for environmental testing laboratories is the documented training program. A training program is essential in evaluating a radiological laboratory because the personnel are usually trained on the job, and the methods that are being performed are sometimes unique to that particular laboratory. A Health and Safety Training Program should be administered to the new employee as part of the orientation process, and this should be documented. The subsequent laboratory training program consists of a period of time where an apprenticeship is completed with an experienced member of the laboratory. Then a series of blanks and blank spikes are analyzed. These results are then reviewed by the laboratory management. If the blanks and blank spikes are analyzed successfully, the employee is then approved to perform that particular analysis. All approvals, with dates and signatures, are documented in the employees permanent training record.

The QAP should also contain a section listing information on the laboratory facilities. The information should include data on instrumentation, data management system, lab size, number of hoods and bench space. The data on instrumentation should note which instruments are under service contract. From this data, a determination can be made regarding the laboratory's capacity, capabilities and potential for down time.

Since the analytical methods that many radiochemical laboratories use are not standardized, the laboratory's radiochemical methods need to be addressed in the QAP. These methods can be broken down into two different categories: standardized methods and performance-based methods. The standardized methods are taken primarily from EPA drinking water/wastewater methods such as EPA-600/4-80-032 (2), and SW-846, (1), or from national laboratory research-grade method manuals such as HASL-300 (4). These methods are widely accepted and many clients request these methods. Performance-based methods are those developed by the individual laboratories and tested with a series of blanks and blank spikes. They are usually taken from various publications or the DOE Methods Compendium and modified to fit the needs of a production laboratory. The performance data should be documented and available for examination.

The QAP should list the radiological parameters and the methods that are used to analyze for them. For all methods, Standard Operating Procedures (SOPs) need to be established. These are critical for the analyst to have at the bench level. The SOPs need to be under a central document control system, and every analyst should be required to sign off that he or she has received the SOP, read and understood it, and agrees to abide by it. Since some laboratories devote a lot of time and money to method development, many such SOPs are proprietary. The Methods of Analysis section below explores this subject in more detail.

The QAP should also include a section on data reporting. Following review by one of the laboratory staff, all the reports that are generated should be reviewed independently by a second person that was not involved in the analyses. Ideally, the laboratory manager should review all the data, but sometimes this is not possible, so this second review should be done by a senior member of the staff that did not perform the analyses. The QAP should also contain a discussion of the various styles/levels of reports that are available. Some of the drinking water reports contain simply the analysis results and the Chains-of-Custody, but some of the DOE/DOD analyses require extensive forms, electronic deliverables and detailed supporting documentation. The analyses cost will vary considerably depending on which type of report is chosen. The QAP should also discuss the data package storage time.

The laboratory's QC requirements should also be listed in the QAP. The basic QC analyses that should be performed for a radioanalytical project are a blank, blank spike and duplicate, each of which should be run at a frequency of 5%. In some instances a matrix spike will also be required, also at a frequency of 5%. The acceptance criteria for these QC parameters must also be listed in the QAP. QC analyses are critical because they demonstrate that the laboratory is in control for the analyses that are performed. The results of the QC analyses should be plotted on control charts to monitor any trends.

There should be a section in the QAP that outlines the initial and continuing calibrations of all radiological counting instruments. This should include the frequency of backgrounds, system performance checks, calibrations, quench curves, self-absorption curves and high-voltage plateaus. These important checks ensure that the counting instrumentation is producing acceptable data.

The QAP should also include a list of personnel resumes. Verifying that the staff of a radioanalytical laboratory is well qualified is a very important part of selecting a laboratory (see section on Qualified Personnel).

The QAP is a critical document that must be reviewed in great detail before selecting a radioanalytical laboratory. An on-site audit should be performed to make sure that the laboratory is actually performing all the items in the QAP.

METHODS OF ANALYSIS

The most challenging phase of radiological analysis is often the radiochemical separation. For the full service radioanalytical laboratory, an extremely wide range of analyses must be offered in order to respond to the variety of requests, including analyses of drinking water, radioactive mill tailings, DOE waste sites, waste water, medical waste and nuclear power plant effluent. A large number of radionuclides are targeted; ^{3}H, ^{14}C, ^{55}Fe, ^{59}Fe, ^{63}Ni, ^{60}Co, ^{89}Sr, ^{90}Sr, ^{99}Tc, ^{129}I, ^{131}I, ^{137}Cs, ^{210}Pb, ^{210}Po, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{228}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am and ^{242}Cm are just some of these. Additionally, many types of matrices are encountered, including water, sludge, soil, rock, resins, filters, cartridges, vegetation, metal and cloth, to name a few. The preparation of many of these matrices for analyses of their constituent radionuclides is a specific, often laborious process. Currently, there is a great lack of method standardization in the industry and methods vary significantly from laboratory to laboratory (see section above on QAP).

Many radiochemical methods in the literature are cumbersome and lengthy, designed to elicit near-quantitative yields and extremely accurate results (within a few percent). For the most part, these are not appropriate for use in the radioanalytical service laboratory, due to the necessity for as rapid a turnaround time as possible. Typically, closely monitored chemical recoveries of 50% or greater are acceptable. Methods should be accurate to within 20%, the accepted standard for blank spike recoveries. These somewhat relaxed constraints allow for the use of a rapid radiochemical method which still meets the required criterion for typical service analyses.

This is not to say that the technical demands of radiochemical analyses are not rigorous. Quite to the contrary, since one is often dealing with radionuclides present at levels of 10^{-12} grams or less per sample, careful radiochemistry is required to avoid serious yield losses. Radioactive yield tracers should be employed whenever possible to monitor recoveries. For example, when performing a $^{234}U/^{238}U$ analysis by radiochemical separation and alpha spectroscopy, samples can be spiked with a ^{232}U tracer (also an alpha emitter). The resultant alpha spectra will contain a fully resolved ^{232}U peak for yield calculation. In some instances, the use of a radioactive tracer will not be possible, due to either its unavailability or potential interferences. In such cases, the yield is generally monitored by adding a nonradioactive carrier of the same element (Sr carrier for ^{90}Sr analyses, for example) and measuring its recovery gravimetrically.

Here, the analyst must exercise extreme caution that the separation is pure, containing no excess precipitate which would add to the recovered carrier weight and compromise the yield correction.

Another potential pitfall in radiochemical analyses is cross-contamination. This is especially serious with regard to samples with low levels of activity, where even a minor amount of contamination can lead to significant errors. Extreme care must be taken to prevent crossover from blank spikes to samples; common sources of such cross-contamination are stirring rods and pipette tips. Pipetting directly out of reagent bottles should be avoided. In addition, all glassware which is reused for analysis should be soaked for at least several hours in 1:1 HNO_3 to remove all traces of activity. Blank samples for each type of analysis the lab performs should be evaluated on a continual basis for any signs of process contamination.

The radiochemical specificity of a given method is absolutely essential. The presence of an extraneous radionuclide in the final source to be counted can add significantly to the detected activity and thus seriously impair the accuracy of the analysis. Therefore, the specificity of each method employed by a radioanalytical laboratory should be determined.

One particularly troublesome area of radiochemical analysis is the preparation of thin, uniform sources for alpha spectroscopy. The two prevalent methods for doing this, electrodeposition and precipitate mounting (e.g., neodymium fluoride), are both laden with potential difficulty. Typical problems encountered are highly variable yields, lack of significant recovery, overly lengthy preparation times and excessively thick sources. A satisfactory method should effectively eliminate these problems and should be routinely useable by any radiochemical laboratory technician. The failing of the radiochemistry laboratory to provide good, accurate analyses for isotopic uranium, isotopic thorium, plutonium, neptunium and americium can usually be traced to poor alpha spectroscopy source preparation.

Since many of these radiochemical methods entail comprehensive wet chemistry, turnaround times are, for the most part, longer than those in conventional organic/inorganic analyses. Some methods, such as tritium in water, gamma spectroscopy and gross alpha/beta, can be done with minimal preparation time, and the turnaround times for these can be as short as one to two weeks. Analyses which require more extensive radiochemical separations or in-growth times will take longer, from 30 to 45 days, depending on the type of reporting requirements. A laboratory performing at turnaround times of 60 days or greater is overloaded with samples.

It should be noted that there are a great number of unique radiochemistry procedures which embody the working list for a radioanalytical laboratory. Each of these must be mastered by that lab; this roster of procedures might easily exceed fifty separate, distinct methods with unique challenges and difficulties.

A radioanalytical laboratory is only as good as the methods of analysis it uses. A firm selecting a lab for use would do well to examine in detail the performance of the radiochemical methods employed by that laboratory.

RADIATION LICENSE

During the process of selecting a radioanalytical laboratory, one important area of evaluation is the radiation license which a given laboratory possesses. With regard to this, there are a number of key aspects to be considered.

First and foremost is the important question of whether or not the lab is in fact licensed to receive, handle and store the radionuclides under consideration. Each radioanalytical lab must by law be so licensed, either directly with the U.S. Nuclear Regulatory Commission or, if the state where the

laboratory is located is an agreement state, with the appropriate state agency.

Secondly, if the lab is licensed for the radionuclides of interest for the proposed analyses, what are the maximum activity levels for each of these radionuclides which the lab can possess at any given time? These levels should be spelled out in the license. Care should be taken to examine these levels to ensure that the anticipated activities of the samples to be sent to the lab do not exceed its license limit.

For those firms dealing with mixed waste, attention should also be given to the disposal of excess samples and extracts/digestates qualifying as mixed waste (containing both hazardous waste as defined by Resource Conservation Recovery Act and radioactive waste as defined by the Atomic Energy Act of 1954). There are at present few facilities able to accept such wastes for disposal. Thus, many radioanalytical labs must, as specified in their license, return such wastes back to the firm which sent them the samples. As more mixed waste disposal facilities come on line, this situation will be ameliorated, but currently, it is still an important issue.

Inquiry should be made as to whether or not the laboratory under consideration screens the incoming samples. Many licensing bodies insist on this, particularly with respect to gamma screening, as a safety monitor. If a radioanalytical facility does perform such screening, it is important to ascertain what the cutoff activity levels are for a sample shipping container to be allowed into that laboratory. Such levels are frequently specified on the radiation license.

LABORATORY FACILITIES

An in-depth examination of a prospective radioanalytical laboratory's facilities is an important part of the evaluation process. A lab which is inadequately equipped will not be able to produce the requisite analyses in the time constraints necessary, and may in addition deliver poor-quality data. These facilities fall under two major headings: radioactivity counting equipment and radiochemistry laboratory facilities.

The fully furnished radioactivity counting room should contain, at a minimum, the following instrumentation hardware: At least two high purity Ge detectors (HPGe) or Ge(Li) detectors for gamma spectroscopy; a minimum of 12 alpha spectrometers; one liquid scintillation counter; a low-background alpha/beta counter with at least four simultaneous detectors; a minimum of three Lucas Cell scintillation counters. Another useful option would be a NaI detector for gamma detection.

The HPGe or Ge(Li) detectors provide high-resolution gamma counting for a variety of matrices. To ensure low x-ray and gamma backgrounds, these detectors should be encased in a 2-inch lead shield with a tin/copper liner. The detector itself must be equipped with a cryostat and dewar to maintain liquid nitrogen temperature. The HpGe or Ge(Li) should be able to detect gammas ranging from 40 to 2000 KeV. Detectors should have a relative efficiency of 25% or greater and a resolution in Full Width Half Maximum (FWHM) of 1.4 KeV or less at 122 KeV and 2.5 KeV or less at 1332 KeV (i.e., the higher the detector's relative efficiency, the greater the FWHM).

Alpha spectrometers should have an active area of at least 450 mm^2, with a minimum resolution of less than 22 KeV FWHM. Backgrounds should be maintained at less than 25 counts per 60,000 seconds, with no visible peak definition. The spectrometers should be equipped with a pulser for daily checks of energy and resolution. The vacuum pump, with manifold, must be able to keep the detectors at less than 60 μm of Hg.

The liquid scintillation counter should be fully programmable, with protocol settings for count time, count cycles, cpm/dpm, quench curve generation and plotting, count windows, count terminators,

background subtraction, half-life correction, quench indicators, static control, color quench correction, luminescence correction, and heterogeneity monitoring. Low background and alpha/beta counting options are desirable. Capacity of the instrument should be 300 samples or greater.

It is preferred that the low-background alpha/beta counter be a multi-detector unit for simultaneous counting of four or more samples at one time. Detector backgrounds should be less than 1 cpm alpha and 3 cpm beta over their long-term use. Efficiencies should be greater than 15% for alpha (^{241}Am) and 29% for beta (^{137}Cs) in a 2 in. planchet geometry.

Lucas cell scintillation counters should contain a 2-inch photomultiplier tube with a light-tight cover of sufficient dimensions to house a standard Lucas scintillation cell with a diameter of two inches and a height of approximately 5 in. The high voltage should automatically be disconnected when the cover is removed.

The computer hardware/software support system for the above counting instrumentation should be user-friendly and menu-driven for ease and quickness of use, and should facilitate the storage of all QC checks, which can then be displayed or printed out in a control chart format. The software should contain complete programs for detector calibration. In addition, the software package should also address all necessary data calculations including carrier, tracer and spike recoveries, efficiency corrections, background subtraction, unit conversion and weight/volume correction.

Important features of the radiochemistry laboratory facility include proper fume hoods and ducting system, sufficient bench and storage space, adequate laboratory equipment, and an extensive stock of the necessary chemicals, solvents, radioactive tracers, etc.

Since many of the radiochemical analyses are performed in strongly acidic media, it is extremely important that the laboratory be equipped with fume hoods which are thoroughly resistant to corrosion. The interior of the hoods should be constructed entirely of polyvinylchloride (PVC). Baffle bolts, nozzles, etc. should also be PVC, or at least, well coated with an acid-resistant material. Due to the fact that acidic vapors frequently condense in the rear wall of the hood, up into the outlet, a wash-down feature with an interior drain is strongly recommended. All hood duct-work should also be PVC. The installation of an acid scrubber unit, upstream from the High Efficiency Particulate Air (HEPA) filters in the hood ventilation system, is vital to the prevention of severe filter corrosion.

As radiochemistry procedures are very wet chemistry intensive, adequate bench space is a must. Benches should be epoxy-type, for chemical and acid resistivity. Sufficient drawer space and wall cabinets for storage of supplies prevents crowding of valuable work space on the bench tops. The laboratory should also have requisite storage area for sample bottles. There should be an adequate number of sinks, preferably with acid traps in the drain system, and a DI water system with outlets at every sink. Additionally, there should be sufficient power available to the lab, with an extensive bank of outlets, to accommodate multiple use of hot plates, centrifuges, pumps, etc.

The variety of radiochemical procedures encountered require that the facility be furnished with an extensive array of laboratory equipment. A large number of hot plates, IR lamps, centrifuges and filtration pumps are needed. The lab should also be equipped with drying ovens, voluminous acid baths for glassware soaking, a muffle furnace, large desiccators, heating mantles and analytical balances. The stock of glassware should be extensive; all sizes of beakers, round-bottom and Erlenmeyer flasks, reagent bottles, volumetric flasks, centrifuge tubes, condensers, vials, etc. should be in immediate access. All necessary safety equipment, including gloves, face shields, safety glasses, lab coats, aprons and spill kits should be present in ample supply within the confines of the laboratory.

A considerable stock of chemicals and solvents are required. These need to be stored in sufficient

supply as to prevent delays in sample analysis during busy times. In addition, an inventory of all required radioactive tracers needs to be continually maintained. These can be very difficult to keep in supply apart from advanced planning, since many such tracers and standards are manufactured only every few years. Where possible, these should be traceable, preferably directly, to the National Institute of Standards and Technology. Radioisotopes with short half lives will need to be periodically replaced.

CLIENT SERVICES/PROJECT MANAGEMENT

A good client services/project management group is essential to prompt communication between the client and laboratory. During a typical project, many deviations from the original work statement are often necessary at the sampling site. These changes must be hastily relayed to the laboratory so that the correct analyses, QC, etc. will be done.

At the inception of a project, a client will sometimes need to have sample bottles sent to the field crews. The bottle type, volume requirements and preservatives are essential to the final data quality. Lacking the proper volume, the sensitivity of the methods is compromised, and if no preservative is added, the integrity of the sample is seriously in question. Since communication of these items is generally handled through client services/project management, each representative must be familiar with the volume and preservative requirements of the radiological laboratory.

During the interim of a project, work scope changes, additional questions, etc. are best coordinated through a client service representative/project manager. This gives the client one point of contact and avoids confusion. Since radiological analysis is more specialized, the client services representative or project manager will need to have some training in this area. This training does not need to be in-depth, but it needs to be sufficient enough to enable the representative to answer the less complex questions and to know as well the proper questions to ask. Having a trained client services/project management staff can greatly facilitate quick answers to many inquiries, while more complex and technical questions can be promptly routed to the radiological laboratory.

The client services/project management personnel also need to follow up on any questions the client has regarding the analyses data. For this reason, their close familiarity with the radiological laboratory data packages is vital. Again, any technical inquiries can be forwarded to the laboratory.

The client services/project management representative is an important link between the customer and the radiological laboratory. When choosing a radioanalytical laboratory, a knowledgeable staff is a must for effective communication. The staff should be well trained and able to answer the simpler radiological questions. Be sure that any changes communicated to a client services representative/project manager are documented. There is nothing more frustrating than making an important change to a sample analysis protocol and having it end up lost or forgotten.

CONCLUSION

The selection of a radioanalytical laboratory should be made only after a detailed assessment of the above considerations. Care should be exercised to pick a lab with the requisite experience, proper quality assurance, expedient and accurate methods with good chemical specificity, the necessary radiation license, superior facilities and a quick, responsive client services/project management group. There is no substitute for quality analytical results. An indifferent approach to this selection process could lead to serious difficulties.

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MANAGEMENT OF LABORATORY RADIOACTIVE AND MIXED WASTE GENERATED VIA ANALYSIS OF DOE SAMPLES

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ABSTRACT. This paper identifies uncertainties associated with an order of U.S.Department of Energy (DOE) which mandates the return of analytical samples to the facility where the sample originated, for disposal. This order has been interpreted differently by various DOE facilities. This paper recommends that a task force be established to resolve this issue.

INTRODUCTION

The management of Mixed Waste derived from U.S. Department of Energy (DOE) samples by the commercial laboratory industry presents unique operational challenges. The Clemson Technical Center (CTC) was established to develop techniques for proper characterization and treatment of radioactive mixed waste including the necessary analytical support services. This paper identifies unsolved issues dealing with interpretation and implementation of order 5820.2A (1) of DOE.

The resolution of this issue is vital to both the DOE and the commercial laboratory industry in order to prevent future interpretations contrary to those presently being implemented, resulting in "Potentially Responsible Parties" if future remediation actions are necessary at the chosen ultimate waste disposal site.

DOE Order 5820.2A was issued to facilitate the proper disposal and accountability of all DOE generated radioactive materials. Specifically, it states that radioactive materials generated by the DOE must be disposed at a DOE site. Relevant sections of the DOE order are as follows.

- "DOE-low-level waste shall be disposed of on the site at which it is generated, if practical, or if on-site disposal capacity is not available, at another DOE disposal facility."
- "DOE-low-level waste that contains non-radioactive hazardous waste components (mixed waste) shall conform to the requirements of this order, applicable DOE Orders, and shall also be regulated by the appropriate regional authorities under the Resource Conservation and Recovery Act."

EXISTING INTERPRETATION AND IMPLEMENTATION

The interpretation and implementation of the DOE Order have been delegated to the various DOE Site Management and Operational organizations(M&O), as approved by the Regional DOE Management groups. This fragmented approach toward interpretation has resulted in various interpretations. The M&O are commercial companies which have been awarded the contract to manage DOE site investigation and remediation. The M&Os develop analytical contracts which contain Statements of Work outlining the responsibilities of the commercial laboratory relative to management of the waste materials generated from the analytical process.

Presently there appears to be consistent interpretation relative to the left-over or unused sample portions. All of the contracts require the return of this sample material to the DOE site of origin. The issue arises as to the interpretation of how to dispose of the analytical residuals resulting from the analytical process, such as spent or leftover Toxicity Charasteric Leaching Procedure leachate, aqueous fraction from Pesticide analysis, and waste from performing a pH measurement.

The CTC has observed the following varied interpretations in contracts presented by M&Os relative to the analytical residuals:

(1) Requires the return of all analytical waste coming into contact with the sample.
(2) Requires the return of any analytical waste containing radioactivity above background.
(3) Will accept the return of analytical waste containing radioactivity >2000 pCi/L.
(4) Will not accept the return of any analytical waste whether it is radioactive or not.

Two of these interpretations (3 & 4) leave the commercial laboratory with an unacceptable scenario for implementation, and at the same time, to remain in compliance with DOE Order 5820.2A.

If the analytical sample contains radioactive materials from a DOE complex, then the resulting analytical residues will potentially contain the same radionuclides resulting in a Radioactive or Mixed Waste for disposal, subject to DOE Order 5820.2A.

The lack of willingness to accept return of the DOE radionuclides in the analytical residues on the part of the M&O organizations and the Regional DOE Management appears to be due to the following reasons:

- The DOE Site may not have the proper permits from the U.S.Environmental Protection Agency as required by Resource Conservation and Recovery Act (RCRA) to accept back the Hazardous waste materials
- The Regional or State governing organizations may be prohibiting the acceptance of new Hazardous Waste into the DOE Site.
- The M&O organization may not have the systems/operations in place to manage the acceptance of new Hazardous Waste.
- The commercial laboratory may not have demonstrated the ability to properly segregate and return the appropriate materials

POTENTIAL RESOLUTION SCENARIOS

The CTC has developed and implemented practices which may provide the M&O organizations the ability to fully implement the DOE Order:

- The commercial laboratory has the ability to implement and execute a waste analysis plan(2) as set forth in 40 CFR Part 268.7(a)(4). A Waste Analysis Plan enables the laboratory to perform on-site treatment of the secondary waste materials within the 90 day accumulation period.This action will remove the potential barrier which may exist relative to returning Hazardous Waste containing radioactivity by eliminating the necessity of RCRA permitting at the DOE site.

- The operational procedures providing segregation of DOE site radionuclides by customer and waste type have been developed and proven effective (i.e., Non-Hazardous water, Acid Waste, Contact Debris, etc.). This type segregation program ensures that the DOE Site will receive back only radionuclides from their facility not other facilities.

CONCLUSION

The DOE has established that it requires responsible management and disposal of DOE generated radionuclides at a DOE site. Presently it is not clear that all of the analytical contracts and Statements of Work being presented to the commercial laboratory industry are consistent with this directive. A uniform consistent interpretation guided by DOE arrangement is required to effectively prevent unforeseen future problems generated by erratic interpretations from site to site.

The ultimate resolution of this issue has to be made on a national level and implemented across the Regions. The commercial laboratory industry has demonstrated its ability to adapt and respond to an ever changing regulatory environment in a compliant manner.

It may become necessary that a special task force is established consisting of the DOE Laboratory Management Division, the M&O contractors, and a representative from the commercial laboratories to develop and propose draft policies to address this important issue.

REFERENCE

1. DOE (U.S. Department of Energy), Radioactive Waste Management, DOE order 58200214, DOE, Washington, DC
2. EPA (U.S. Environmental Protection Agency), Land Disposal Restrictions, 40 CFR 268, U.S. Government Printing Office, Washington, DC (1992).

CHAPTER 9

Storage and Disposal

SURVEY OF INTERMENT TECHNOLOGIES FOR MIXED LOW LEVEL WASTE AT DOE FACILITIES

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ABSTRACT. The siting, design, construction, operation, and closure of mixed waste disposal facilities at Federal facilities must adhere to the requirements of the Resource Conservation and Recovery Act (RCRA) and applicable Department of Energy (DOE) Orders. The hazardous component of mixed waste is regulated under RCRA while the radioactive component of mixed waste at DOE facilities is regulated under the Atomic Energy Act through DOE Orders.

Commercial low level waste (LLW) disposal permitted by the Nuclear Regulatory Commission (NRC) has historically used shallow land burial as the primary LLW interment technology. However, the Low Level Radioactive Waste Policy Amendments Act (LLRWPAA) of 1985 required the NRC to identify alternative methods for the disposal of LLW other than shallow land burial. As part of the LLRWPAA, the DOE was required to aid in the development of LLW disposal alternatives. Greater-confinement disposal (GCD) technologies were developed in response to the requirements of the LLWRPAA. GCD technologies are defined as techniques that use natural and/or engineered barriers and provide a greater degree of isolation than that of shallow land burial (1).

This paper reviews DOE identified GCD technologies including below ground vaults, above ground vaults, modular concrete canister disposal, and earth-mounded concrete bunkers in relation to the adaptability of the technology to incorporating RCRA land based unit design requirements.

BACKGROUND

The Nuclear Regulatory Commission (NRC) and the Environmental Protection Agency (EPA) jointly developed the National Profile on Commercially Generated Low-Level Radioactive Mixed Waste (the National Profile) to address uncertainty in the volume, generation rate, and characteristics of mixed waste. The study confirmed that commercial generation is a small fraction of the amount generated by Department of Energy (DOE) facilities. The stored inventory as of 1990 is approximately 70,000 m^3 and the annual generation rate is approximately 8000 m^3 (2). Currently, limited treatment and storage options exist for mixed waste streams. Although the National Profile concludes that adequate treatment capacity exists for most commercially generated mixed waste, commercial treatment of DOE mixed waste may pose a significant deficiency in the treatment capacity for current treatment facilities. Therefore, DOE must consider additional mixed waste management options at DOE operated facilities. Treatment options are available at some DOE facilities; however, in many cases, certain fractions of mixed waste may ultimately require disposal.

The Nevada Test Site and the Waste Isolation Pilot Plant are each pursuing mixed waste retrievable storage and subsequent permanent disposal. Still other avenues of disposal should be considered to lower the risk/hazard ratio through Greater-confinement dispsoal (GCD) technologies (5) and to thwart public concern over transportation accidents and potential corrective actions resulting from shallow land burial (SLB).

REGULATORY OVERVIEW

The disposal of mixed waste is governed primarily by two federal laws. The hazardous component is regulated under Resource Conservation and Recovery Act (RCRA) and the radioactive component is regulated under the Atomic Energy Act (AEA). The AEA authorizes the DOE to regulate radioactive material at DOE facilities. DOE administers this authority through enforceable orders. The EPA administers the RCRA program through regulations specified in Title 40 of the Code of Federal Regulations (40 CFR) Sections 260-281 (6). However, the RCRA program was designed to authorize states to implement the program by developing regulations equivalent to or more stringent than those specified in the applicable sections of 40 CFR.

Atomic Energy Act

DOE administers their authority under the AEA through enforceable orders. DOE is specifically exempt from the NRC regulations promulgated pursuant to the AEA except as specified in the Energy Reorganization Act of 1974. DOE Orders are the basis for establishing policy and guidelines for non-AEA issues such as hazardous waste management and, therefore, mixed waste management. The DOE Orders most significant to a Mixed Waste Disposal Facilities (MWDF) include:

- Order 5480.4 Environmental Protection, Safety, and Health Protection Standards
- Order 5400.3 Hazardous and Radioactive Mixed Waste Program
- Order 5820.2A Radioactive Waste Management

Order 5480.4, issued on May 15, 1984, establishes the requirements for implementing the mandatory environmental protection, safety, and health standards (7). This order states that RCRA regulations are a statutory requirement at DOE facilities except for activities conducted under the authority of the AEA. However, this same order establishes the DOE policy that RCRA is mandatory for activities conducted under the AEA which involve hazardous waste. Therefore, DOE policy is to comply with RCRA requirements in the management of mixed waste.

Order 5400.3 defines the policy of DOE to manage all mixed waste according to RCRA and the AEA (8). RCRA applies to mixed waste management unless it is inconsistent with the AEA. This order also states that the radioactive component of mixed waste must be managed in accordance with DOE Order 5820.2A.

The primary DOE Order defining performance standards for a radioactive waste disposal facility is Order 5820.2A, Radioactive Waste Management (1). The purpose of Order 5820.2A is "to establish policies, guidelines, and minimum requirements by which the DOE manages its radioactive and mixed waste...". The order contains detailed, specific requirements for all radioactive waste generators and treatment, storage, or disposal (TSD) facilities. DOE Order 5820.2A requires that LLW and mixed waste with a low-level radioactive component be managed to meet the following performance objectives:

- Protect public health and safety in accordance with DOE specified standards.
- Assure that external exposure to the waste and concentrations of radioactive material which may be released into environmental media, plants, and animals results in an effective dose equivalent that does not exceed 25 mrem/yr to any member of the public.
- Meet the requirements of the National Emissions Standards for Hazardous Air Pollutants (NESHAPs, 40 CFR 61) for releases to the atmosphere (9).
- Maintain releases of radioactivity in effluents to the general environment as low as is reasonably achievable.
- Assure that the committed effective dose equivalents received by inadvertent intruders after 100 years will not exceed 100 mrem/yr for continuous exposure or 500 mrem/yr for a single acute

exposure.

- Protect groundwater resources consistent with regulatory requirements.

Resource Conservation and Recovery Act

The RCRA regulations governing disposal of hazardous waste define stringent siting and permitting standards. The design and operating basis for hazardous waste disposal is effective waste isolation accompanied by systems for detection and collection of potential releases. Design requirements for land disposal units include installation of two liners below the waste unit and leachate collection systems above and between the liners (9). Figure 1 presents a typical schematic of the required double liner and leachate collection system for land-based disposal. Additional design requirements for land-based disposal units include run-on and run-off control systems each equipped with a collection system. A wind dispersion control mechanism is also required as part of RCRA.

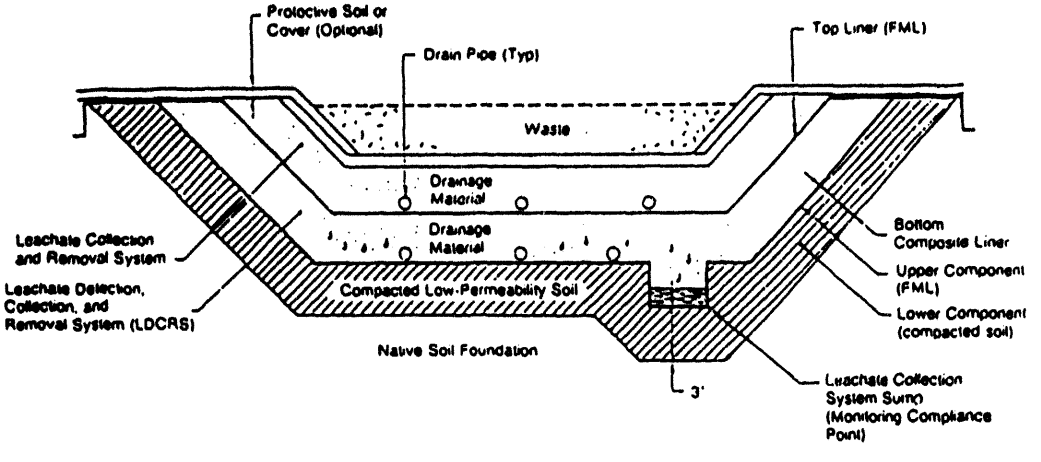


Figure.1 Schematic of a double liner and leachate system as required under RCRA(12)

Closure of a RCRA permitted land-based unit, specifically landfills and surface impoundments, must satisfy the RCRA requirements promulgated under 40 CFR 264. One of the primary closure requirements is installation of a RCRA cap. EPA has issued guidance on the design of final covers in the document entitled "Final Covers on Hazardous Waste Landfills and Surface Impoundments" (10). The final cover recommended in the guidance document is a multilayer design comprised as follows:

- A top layer consisting of two components: (a) either a vegetated or armored surface component, selected to minimize erosion and, to the extent possible, promote drainage off the cover, and (b) a soil component with a minimum thickness of 60 cm (24 in.), comprised of topsoil and/or fill soil as appropriate.
- Either a soil drainage (and flexible membrane liner (FML)-protective bedding) layer that will

effectively minimize water infiltration into the low-permeability layer, or a drainage layer consisting of geosynthetic materials with equivalent performance characteristics.

- A two-component low-permeability layer, lying wholly below the frost zone, that provides long-term minimization of water infiltration into the underlying wastes, consisting of a FML component, a compacted soil component, and a maximum in-place saturated hydraulic conductivity of 1×10^{-7} cm/sec.

The general closure performance standards specified in 40 CFR 264 state that disposal units must be closed in a manner that minimizes the need for further maintenance. A 30 year post closure care period for land-based disposal units is required by RCRA regulations. The post closure care period may be extended or reduced by an authorized State as warranted by unit specific conditions.

SURVEY OF INTERMENT TECHNOLOGIES

Greater-confinement interment technologies for LLW disposal incorporate design features to meet the performance objectives as defined in DOE Order 5820.2A. The design basis for these interment technologies is governed primarily by the concept of waste isolation. The waste should be isolated such that the associated radioactivity is given sufficient time to decay to a level at which no member of the public would be exposed to an effective dose equivalent above that specified in the performance objectives (25 mrem/yr)(1). The DOE requires a 5 year post closure care period and an institutional control period of 100 years for LLW disposal facilities (1).

Description and Performance of Interment Technologies

This section provides descriptions of the GCD technologies. A complete performance assessment of the described interment technologies is beyond the scope of this project. However, an evaluation of the interment technologies is provided based on a conceptual design report entitled "Alternative Concepts for Low-Level Radioactive Waste Disposal" (Alternatives Concept Report) (11). This report was developed by the DOE National Low-Level Radioactive Waste Management Program to assist states and regions in developing new LLW disposal methods in accordance with the requirements of the LLRWPAA. The Alternatives Concept Report evaluates six alternatives including:

- shallow land burial (SLB)
- intermediate depth disposal (IDD)
- below-ground vault (BGV)
- above-ground vault (AGV)
- modular concrete canister disposal (MCCD)
- earth-mounded concrete bunker (EMCB)

Only GCD technologies are being considered for this paper. Therefore, SLB will not be discussed further. Although IDD is considered a GCD technology, the hazardous component of mixed waste would generally not be allowed in this type of landfill. For this reason, IDD will not be considered in this document for use as a mixed waste interment technology.

The aspects of the evaluation as stated in the Alternatives Concept Report:

> The conceptual designs were developed under the same assumptions to ensure a common basis for evaluating and comparing the six disposal concepts. Each of the conceptual facilities were designed to, and evaluated against, the applicable NRC requirements of 10 CFR 61 ... Each disposal facility was designed to handle approximately 235,000 ft^3 of LLW per year over a 30 year operating life, for a

total of about $7x10^6$ ft^3. Waste characteristics and the radioactive source term for the LLW, assumed to be disposed at the conceptual facilities, were based upon information published by the NRC. The waste was assumed to be composed of 95% Class A, 2% Class B, and 3% Class C by volume. It was assumed that the technology would be developed on a generic site that had characteristics typical of a humid location. Furthermore, it was assumed that the site met the siting requirements of 10 CFR 61.

The evaluation presented in the Alternatives Concept Report is not specific to the performance objectives defined under DOE Order 5820.2A. The basis of the evaluation within the Alternatives Concept Report is solely on the disposal of set quantities of commercially generated Class A, B, and C LLW, not DOE generated LLW or mixed waste. However, the evaluation is used within this paper as a means of evaluating the relative performance of each LLW interment technology in terms of managing radioactive waste. For mixed waste management, the evaluation presented in this paper is based on the adaptability of the technology to incorporating RCRA land based unit design requirements.

In addition to the above evaluation, the interment technologies discussed are compared to the EPA/NRC joint guidance for the siting and conceptual design of a commercial mixed waste disposal facility(12). The siting and design concept developed by the EPA and NRC are not promulgated regulations and should only be viewed as guidance. Since no design standards specific to mixed waste disposal facilities currently exist, interment technologies discussed are evaluated according to their ability to meet the EPA/NRC joint conceptual design guidance. The selection of the most technically effective interment technology for siting purposes will, therefore, be based on the overall ability of the technology to satisfy DOE performance objectives and the joint EPA/NRC conceptual design guidance features. In some cases engineering enhancement for a particular interment technology can be used to meet the EPA/NRC guidance design criteria. The features of the EPA/NRC design concept are:

- The waste is placed above natural grade.
- The liner system below the waste extends from below natural grade and at least up to natural grade.
- A leachate collection and removal system is provided below the first liner under the waste.
- A leakage detection and removal system is provided below the second liner under the waste.
- A cover system is placed above the waste to limit water percolation into the disposal unit.

Figure 2 provides an overall view of the conceptual MWDF based on the EPA/NRC guidance criteria. The design concept meets the EPA requirements for the installation of two or more liners and leachate collection systems (9) and the NRC requirement of the minimization of access of water to the waste during disposal operations and following closure (13). In this design concept, a leak detection tank and leachate collection tank are encircled by a berm that controls surface water runoff resulting from precipitation events during operation. The drainage pipes in the upper, primary collection system would collect any leachate that could possibly develop above the top liner and below the emplaced waste. Any leachate collected would drain through pipes to the primary leachate collection tank where the leachate would be tested and treated, if required (12). Any leachate collected by the lower leachate collection and removal system would drain to the leak detection tank (12).

It should be noted that despite the NRC and EPA agreement for above grade mixed waste disposal, the Texas Low-Level Radioactive Waste Disposal Authority has recently reported its intent to dispose all mixed waste below natural grade (14). The final decision for design criteria will be made by the particular State authority or by the DOE.

Modular Concrete Canister Disposal (MCCD). In MCCD, wastes are placed within shallow trenches below natural grade. The wastes are encased in steel-reinforced concrete canisters prior to disposal. In this regard, MCCD provides an additional barrier for releases of radioactivity as compared to SLB. Structural stability

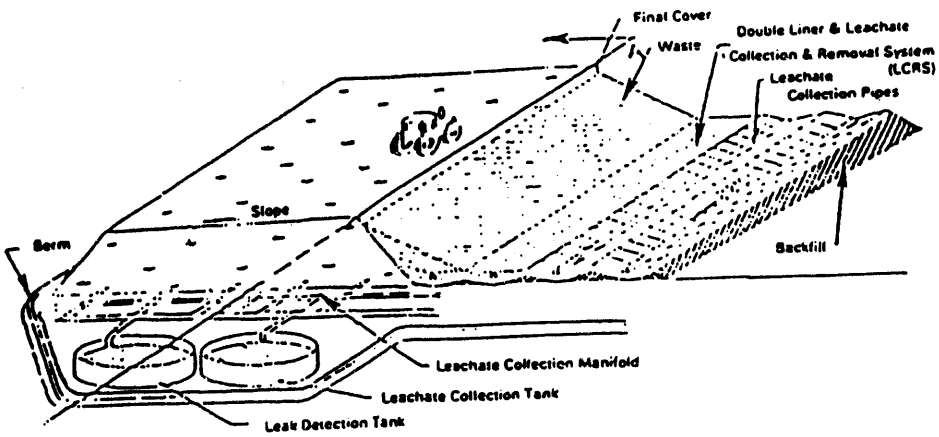


Figure 2. EPA/NRC conceptual mixed waste disposal facility(12)

can be provided by the waste canisters for LLW; however, for mixed waste LDRs would apply. The final waste form for mixed wastes within the canisters would most likely be a stabilized form. Engineered placement of the canisters within the trenches and backfilling with sand provides short term stability during operation.

MCCD trench floors for LLW disposal normally consist of a gravel base which serves to facilitate the removal of water that may accumulate from precipitation occurring during operation. The floors would normally be sloped to a French drain system which is used to drain and collect water that enters the disposal unit during operation and following closure. However, in the case of mixed waste disposal, the required avenue of water control is the RCRA double liner and leachate collection system. Therefore for mixed waste disposal, design features for lining and leachate collection would be as described in the EPA/NRC guidance of MWDF design.

Specific cover design requirements for closure of the MCCD unit must, at a minimum, meet RCRA requirements or be demonstrated to do such (9). The NRC requires greater thicknesses for earthen covers when managing Class B and C waste in comparison to managing Class A wastes. Specific thicknesses of cover layers will be based on DOE requirements for the Energy Systems classification of LLW in order to meet DOE performance objectives. For MCCD the principal barrier to radionuclide release is the concrete canister with an additional barrier provided by the earthen cover. Figure 3 presents a typical schematic of MCCD technology.

As required under RCRA, run-on and run-off control systems would be required during construction, operation, and upon and following closure of the disposal unit. Wind dispersion control systems must also be incorporated as a RCRA requirement for the MCCD.

The advantages of MCCD include:

- MCCD trenches are designed to minimize infiltration of surface water and groundwater following closure.
- Long-term active maintenance should be minimal.
- Inadvertent plant, animal, or human intrusion is unlikely due to the cover and additional barrier offered by the waste package.
- Remote handling of high activity wastes can be used to minimize exposure to workers.
- MCCD technology is currently being evaluated for commercial LLW disposal in different states.

The disadvantages of MCCD include:

- MCCD trenches must be protected from flooding during construction and operation.
- MCCD trenches are not amenable to low volume or intermittent operations.
- MCCD are not amenable to visual inspection and monitoring following closure.
- Concrete canisters may be susceptible to weathering.

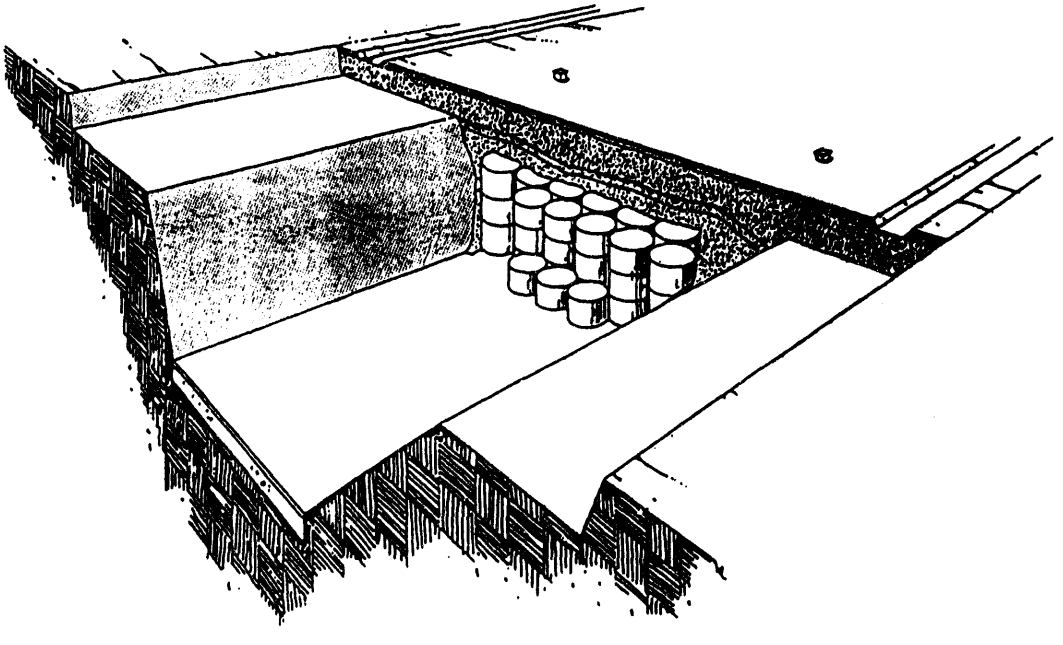


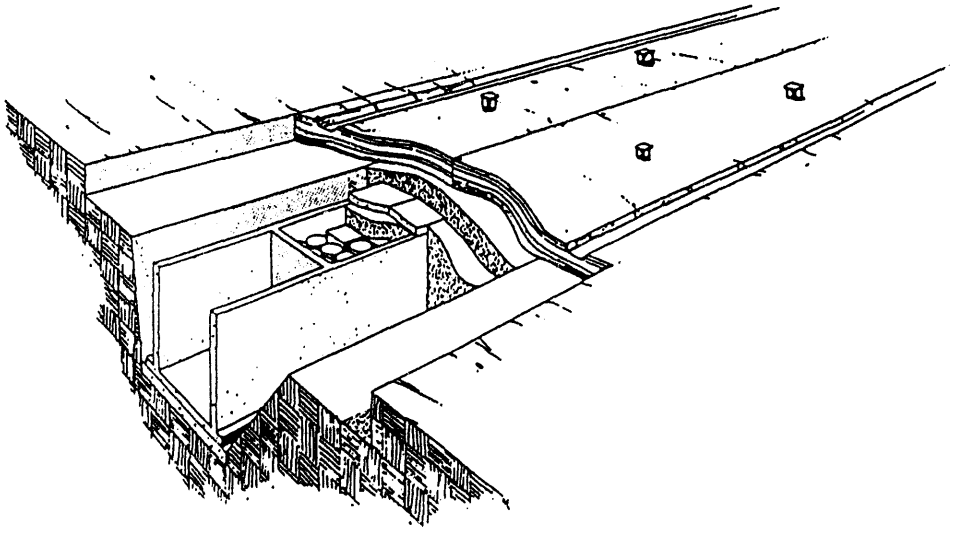
Figure 3. Typical illustration of a modular concrete canister disposal facility(11).

Below-Ground Vault (BGV). BGVs consist of emplacing waste in engineered concrete structures below the natural grade. The structures generally consist of concrete floors, walls, and roofing. As with other below grade interment technologies, earthen covers are used to provide additional barriers against infiltration, to reduce surface radiation levels, and to provide an additional barrier against inadvertent intrusion. Structural stability is provided by the disposal structure itself. Additional stability would be provided through the waste form. Short-term stability during operation is maintained through engineered placement of the waste packages and backfilling with sand.

BGVs are actually composed of a number of different cells that are closed individually as each cell is filled. This design normally reduces the amount of precipitation accumulation within the vault during operation and provides a reduced radiation exposure to operations personnel. The use of run-on and run-off central systems, as required under RCRA, will further minimize the amount of precipitation within the individual cells.

Since BGVs consist of concrete floors and a drainage system, the double liner and leachate collection system required under RCRA would not be appropriate. Exceptions to the double liner and leachate collection system requirements are allowed if alternative design and operating practices, together with location characteristics, are demonstrated to the EPA Regional Administrator to be equally effective in preventing the migration of any hazardous constituent into the groundwater or surface water. Cell floors of the BGV are slightly sloped to floor drains to facilitate drainage of any waste that might enter the unit. Cell drains discharge to a collection sump which is equipped with a monitoring standpipe. It is assumed that any water accumulated within the sump will be actively collected, tested and, if necessary, treated and properly managed during the active institutional control. In this sense the concrete cell floor and drainage, collection, and monitoring system of the BGV could serve as the primary leachate collection system in terms of RCRA requirements. An additional barrier to groundwater infiltration such as a single liner or other engineered containment system could be used to satisfy the RCRA requirements for secondary containment. For BGVs the concrete structure also provides the principal barrier to radionuclide release with an additional barrier provided by the earthen cover. The final covers must meet the minimum standards of RCRA. Specific thicknesses of cover layers must at least meet RCRA requirements or be demonstrated to be effectively equivalent to RCRA standards. However, cover layer thicknesses may vary pending DOE requirements for the isolation of specific classes of LLW.

Run-on and run-off control systems and wind dispersion control mechanisms must be incorporated as part of the construction, operation, closure, and post-closure of BGVs to meet RCRA standards. An illustration of BGVs is presented in Figure 4.



Figere 4. Typical illustration of a below-ground vault facility(11).

Advantages of BGVs include (15):

- BGVs are visually unobtrusive.
- BGVs are generally not susceptible to damage or exposure of waste packages from erosion, predictable seismic events, surface disturbances, or soil settlement.
- BGVs provide barriers to plant or animal intrusion and inadvertent human intrusion through the soil cover.
- BGVs provide additional barriers to radionuclide migration as compared to SLB.
- BGVs are structurally stable, can support backfilled earth, and do not depend on waste packages for support.
- Long-term active maintenance requirements should be minimal.
- BGVs are currently used for storage purposes in Canada and at the Oak Ridge National Laboratory (ORNL) (16).

Disadvantages of BGVs include:

- BGVs must be protected against flooding during construction and operations.
- BGVs are not amenable to visual inspection and monitoring following closure.
- BGVs are not amenable to remote handling equipment.
- BGVs must be protected from degradation caused by corrosive soils.

Above-Ground Vault (AGV). AGVs consist of emplacement of waste in reinforced concrete structures above the natural grade. The structures are constructed of concrete floors, walls, and roofing and are composed of individual cells. Cells are individually filled with waste packages, backfilled with sand to provide short term stability, and then closed with concrete roofing. AGVs lack earthen covers upon closure and, therefore, rely solely on the engineered structure to prevent radioactivity releases. Should the integrity of the vault be impaired or breached, no additional natural or man-made barriers are present to prevent radionuclide releases in AGV technology.

Cell floors of AGVs are sloped slightly and floor drains are provided to facilitate drainage of any precipitation which may infiltrate the unit during operation. Individual cell drains are normally directed to a collection sump which is actively monitored through standpipes. The double liner and leachate collection system required by RCRA would not be appropriate for management of leachate for AGVs. In addition to the drainage system and collection sump, a secondary containment system consisting of a liner or other engineered devices and a leak detection system may satisfy the RCRA requirements. Exemptions to the double liner and leachate collection system are allowed if the alternate engineered containment and detection system are demonstrated to the EPA.

AGVs may be considered a miscellaneous unit under RCRA standards (40 CFR 264 Subpart X). A final cover meeting RCRA requirements is not required for miscellaneous units. However, AGVs must satisfy the RCRA standards for protection of human health and the environment. The design and operation to meet RCRA requirements must be demonstrated to the EPA. In addition, run-on and run-off control systems and wind dispersion control mechanisms are not specified for RCRA miscellaneous units. However, RCRA specifies that the permitting and provisions required for other RCRA regulated units (i.e., landfills, surface impoundment, tanks, etc.) must be satisfied for miscellaneous units. Again, a demonstration to satisfy these RCRA standards would be required for mixed waste disposal in an AGV. A typical conceptual design of AGVs is presented in Figure 5.

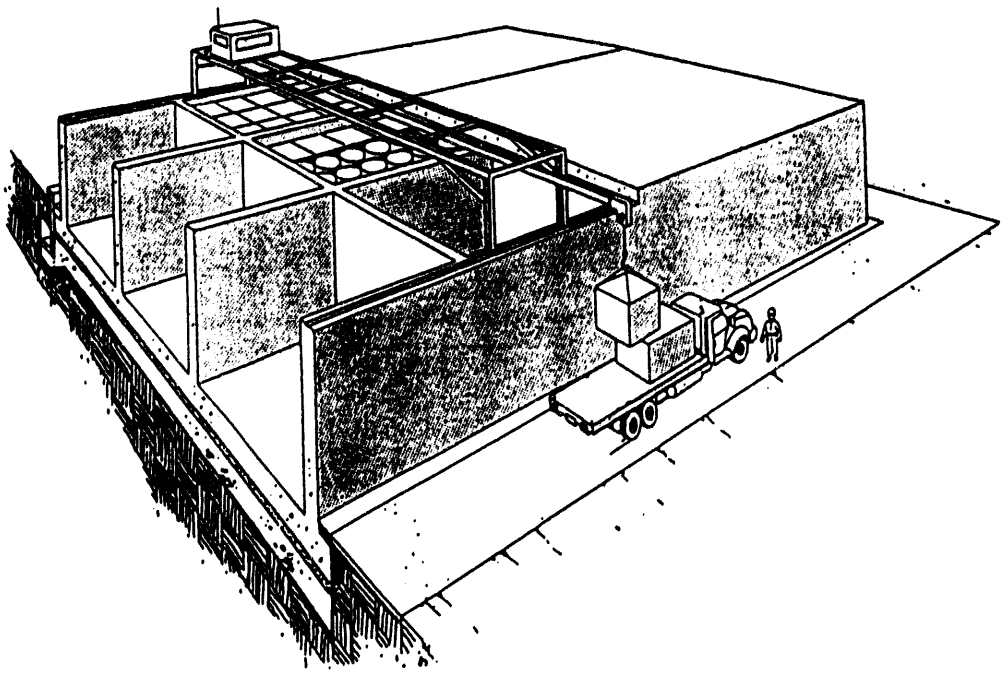


Figure 5. Typical illustration of an above ground vault facility(11).

The advantages of AGVs include (15):

- AGVs do not depend on variable geologic materials for waste isolation.
- AGVs do not rely on the waste packages for support.
- During active institutional control, inadvertent human intrusion is unlikely due to the high visibility and physical security offered by AGVs.
- AGVs are not susceptible to groundwater infiltration.
- AGVs are not susceptible to plant and animal intrusion.
- AGVs can be easily inspected and monitored.
- AGVs are currently used for storage purposes in Canada (16).

The disadvantages of AGVs include:

- AGVs possess no secondary barrier to radionuclide release.
- Insufficient time may be available for remedial actions, if required.
- Active maintenance requirements are likely to be more extensive due to exposure to the elements.
- Exposure of workers to radiation hazards may be high unless temporary shielding is used during operation.

Earth-Mounded Concrete Bunker (EMCB). EMCBs can consist solely of the disposal of waste above grade with an earthen cover (tumulus) or in combination with a below grade concrete bunker for waste classes

requiring greater isolation. Below ground bunkers of the EMCB are similar in most respects to BGVs. The tumulus can be constructed over the concrete bunker. Modular concrete canisters can be used for waste disposal within the tumulus to provide additional stability and a barrier against radioactivity releases. An earthen cover is placed over the tumulus following operational closure of the unit. Short term stability is provided by backfilling with sand around waste packages within the above-grade tumulus. Void spaces within the below-grade bunker are filled with concrete which solidifies to form a concrete monolith. A double liner and leachate collection and detection system, as described for the EPA/NRC MWDF guidance criteria, would be required for management of leachate.

The earthen cover for closure of the tumulus must, at a minimum, satisfy the RCRA requirements. Specific cover layer thicknesses may vary pending DOE requirements for the specific LLW class. As with other land-based RCRA units, a run-on and run-off and wind dispersion control mechanism is required. A typical illustration of an EMCB is presented in Figure 6.

The advantages of EMCBs include (15):

- EMCBs are resistant to infiltration of surface water and groundwater.
- Inadvertent human intrusion is unlikely due to the high visibility and physical barriers offered by EMCBs.
- Long-term active maintenance should be minimal.
- Remote handling of high activity wastes can be readily used to reduce exposure of workers to radiation hazards.
- EMCBs are successfully being used for disposal at the Centre de la Manche site in France (16). EMCBs are also being utilized in Canada for LLW storage purposes (15).
- EMCBs are currently being used for low-level waste disposal at the Oak Ridge Reservation in Oak Ridge, Tennessee.

The disadvantages of EMCBs include:

- EMCBs must be protected from flooding during construction and operation.
- Strict packaging requirements and waste disposal sequencing requirements must be followed during operations.

COMPARISON OF INTERMENT TECHNOLOGIES

Table 1 provides a summary of the capabilities of each interment technology. The capabilities are summarized in relation to the performance objectives discussed in the evaluation report and the EPA/NRC design guidance criteria. Intruder scenarios presented in Table 1 include Intruder-Explorer, Intruder-Construction, and Intruder-Agriculture. Each of these scenarios refers to specific computer model aided predictions described in the Alternatives Concept Report. With the exception of AGVs, each interment technology meets the performances objectives. AGVs exceeded the whole body dose of 25 mrem/yr and a thyroid dose of 75 mrem/yr to any member of the public. The only interment technology that meets all the design guidance criteria of the EPA/NRC agreement is the EMCB.

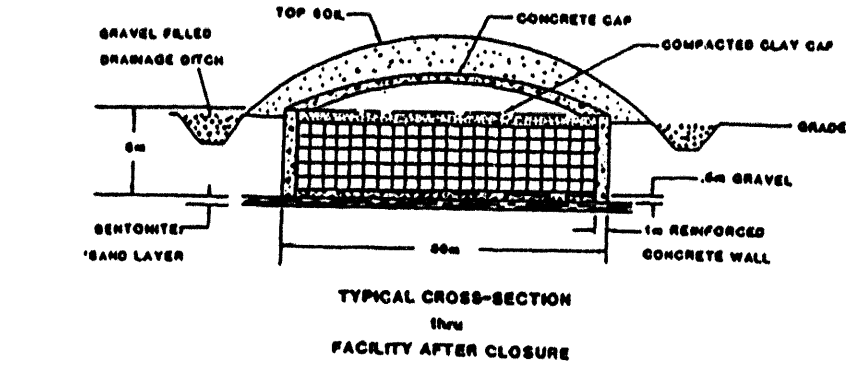
CONCLUSIONS

Based on the relative performance of the LLW interment technologies in relation to the DOE performance objectives and the ability of the technology to incorporate RCRA land-based unit design requirements, the following disposal options provide the most practical GCD technology for mixed waste disposal:

Table 1. Comparison of Interment Technologies.

Performance Criteria	MCCD	BGV	AGV	EMCB
10 CFR 61.41 Protection of General Population				
Whole Body Dose Thyroid Dose	6.5 mrem/yr 40 mrem/yr	4.1 mrem/yr 39 mrem/yr	34 mrem/yr* 330 mrem/yr*	3.4 mrem/yr 33 mrem/yr
10 CFR 61.42 Protection of Inadvertent Intruders				
Intruder - Explorer Intruder - Construction Intruder - Agriculture	Negligible 0.03 mrem/yr 6.7 mrem/yr	Negligible 0.01 mrem/yr 4.1 mrem/yr	20 mrem/yr 0.4 mrem/yr 7.9 mrem/yr	Negligible 0.02 mrem/yr 3.5 mrem/yr
10 CFR 61.43 Protection of Individuals During Operations	16 person - rem/yr	16 person - rem/yr	15 person - rem/yr	14 person - rem/yr
10 CFR 61.44 Long-Term Stability	Provided by Waste Canister	Provided by Vault Structure	Provided by Vault Structure	Provided by Waste Form or Container
NRC/EPA Design Guidance	Below Grade **	Below Grade **	No Cover **	Meets Criteria
40 CFR 264.301 RCRA Double Liner and Leachate Collection System	Able to Meet Design Requirements	Drainage and Collection System, Secondary Containment and Leak Detection System Must be Demonstrated to EPA	Drainage and Collection System, Secondary Containment and Leak Detection System must be Demonstrated to EPA	Able to Meet Requirements
40 CFR 264.301 Run-on/Run-off Control	Able to Meet Design Requirements	Able to Meet Design Requirements	Not Required but Must Be Demonstrated	Able to Meet Design Requirements
40 CFR 264-301 Wind Dispersal Control	Able to Meet Design Requirements	Able to Meet Design Requirements	Not Required but Must Be Demonstrated	Able to meet Design Requirements
40 CFR 264.111 DOE Order 5820.2A Minimize Post-Closure Maintenance	Minimal Due to Engineered Final Cover	Minimal Due to Engineered Final Cover	Active Maintenance Required	Minimal Due to Engineered Final Cover

* Exceeds the NRC Criteria of 25 mrem/yr Allowable Whole Body Dose and the Allowable Dose to the Thyroid of 75 mrem/yr.
** Does Not Meet the NRC/EPA Design Guidance Criteria



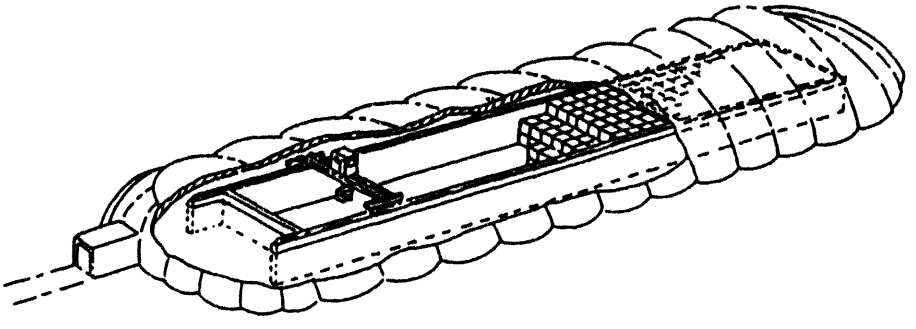


Figure 6. Typical cross-section and illustration of an earth moulded concrete bunker(15).

- EMCB The EMCB provides the greatest degree of performance capability in terms of protection of the public, protection of inadvertent intruders, protection of workers, and long-term stability. EMCBs also meet the EPA/NRC conceptual design guidance criteria.

- BGV Although the BGVs do not meet all of the EPA/NRC conceptual design guidance criteria, BGVs offer a degree of performance capabilities similar to that of EMCBs. The RCRA land based design requirements may pose some difficulties with BGVs; however, demonstrated equivalent systems may be appropriate.

This paper provides a preliminary review of GCD technologies potentially applicable to mixed waste disposal at DOE facilities. The evaluation presented is based on the ability of the particular GCD technology in meeting NRC performance standards and the adaptability of the technology in meeting the RCRA land based design requirements. LLW generated by DOE is much different than that of commercial generation and cannot be directly compared. In addition, the performance objectives designated by DOE differ somewhat from the NRC requirements. Therefore, there is a greater need to conduct additional performance assessments of GCD technologies incorporating RCRA land based requirements for DOE mixed waste streams.

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INNOVATIVE SYSTEMS FOR MIXED WASTE RETRIEVAL AND/OR TREATMENT IN CONFINED SPACES

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ABSTRACT. Some of the Department of Energy (DOE) mixed waste is stored in confined spaces or tanks that are access 'imited. Freeboard space above the waste usually is monitored for temperature, pressure, humidity and/or certain gas concentrations. Access to treat and/or retrieve wastes from these storages is very difficult. Equipment, practical, yet not overdesigned, are usually not available commercially. Applications invariably dictate that the equipment be especially designed to meet the specific requirements.

PARSONS, under contract to the DOE and Fernald Environmental Restoration Management Corporation for the Environmental Remediation Action Project, Fernald Environmental Management Project, Ohio, recently faced two applications of this kind. One requirement was the design of an applicator system for the remote controlled placement of Bentonite slurry over the surface of mixed wastes in two enclosed silos, as a barrier to retard the emanation of radon gas into the freeboard space. Each silo has an inside diam of 24.4 m (80 ft) with accessibility limited to a 500 mm (20-in) center manhole for the application equipment.

The other requirement was to design a remote controlled system to retrieve the wastes from the above silos for treatment. The retrieval system must be safe and reliable, operate at steady high rates and be amenable to automation. The system must be capable of retrieving the waste through small openings without imposing any loads on the containment structures. The system must be capable of virtually total waste removal, thus obviating or minimizing the need for additional equipment.

This paper discusses design/construction features and application specifics of the two systems, such as size of components, method of deployment, operation and controls. The paper also compares qualitatively the two systems, developed by the authors, to other means of abatement and retrieval.

INTRODUCTION

The United States Department of Energy (DOE) Fernald Environmental Management Project (FEMP) is located approximately 32 km (20 mi) northwest of Cincinnati, Ohio. The FEMP established operations in 1951 under orders of the U.S. Atomic Energy Commission and produced uranium and other metals for use at other DOE facilities. Production at the FEMP has ceased, and the environmental remediation of the entire site is ongoing. A part of the sitewide remediation effort is the removal, treatment, and disposal of the K-65 wastes form Silos 1 and 2. These silos contain radium-bearing residues from the processing of pitchblende ore (high grade uranium mineral) at Mallinckrodt Chemical Works and Lake Ontario Ordinance Works (currently known as Niagara Falls Storage Facility).

The silos are constructed of steel-reinforced concrete and are approximately 24.4 ms (80 ft) in diameter, with 8 m (27-ft) high walls, and are 11 m (36 ft) high at the top of the dome.

Age has taken its toll on those silos. The structures have cracked, and some of the concrete has peeled off, exposing rusted and deteriorated reinforcing steel. These conditions have so weakened the silo domes that any contact with the domes, especially the center 9 m (30 ft), is strictly prohibited.

The radioactive constituents of concern in the silos are Uranium-238 and 234, Radium-226, and Thorium-230. The radium-bearing residues emit radiation in the form of alpha, beta, and, in small amounts, gamma rays; radon gas is also emitted. Most of the radon generated was contained within the enclosed silos. About 6 curies of radon were generated and released into the head space of each silo per day, based on a radon emission flux rate of 1.5×10^3 pCi/m^2 sec. Due to the age and condition of the silos, the radon emission from the silos exceeded the United States Environmental Protection Agency (EPA) limits.

These silos were included in one of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Remedial Investigation/Feasibility Studies (RI/FSs) identified as Operable Unit 4 (OU-4), now called CERCLA Resource Conservation and Recovery Act (RCRA) Unit 4 (CRU-4) at the FEMP. While pursuing final remediation, it has been determined by the DOE that a non-time-critical removal action is necessary. The scope of this removal action can be broadly defined as reducing the chronic radon gas emissions to the atmosphere from Silos 1 and 2. This removal action was being conducted pursuant to the Consent Agreement between the DOE and the EPA as Silos 1 and 2 Removal Action. An Engineering Evaluation/Cost Analysis (EE/CA) was prepared to evaluate the removal action alternatives using the preliminary characterization data and select a preferred alternative. The selected alternative consisted of covering the K-65 residues with a gas barrier material that will retard the emanation of radon gas into the space between the residues and the silo dome.

Bentonite was selected as cover material due to its good emanation coefficient, its favorable plasticity, its capability to retain water, and the relative ease by which it can be placed into the silos. PARSONS was retained as design engineers, under DOE Contract, to supply the design/construction packages to carry out the above removal action. Design packages were developed by PARSONS; while procurement, construction, and application were performed by Westinghouse Environmental Management Company of Ohio (WEMCO), then current site manager. All activities were performed and executed successfully in accordance with the requirements of the work plan compiled by PARSONS and WEMCO, and approved by the EPA.

The removal action outlined above can only be described as a stop-gap measure. It was intended to reduce radon gas emission to the atmosphere to a minimum during the long time period required to effect remediation.

The remediation of the K-65 wastes consists of the retrieval and treatment of the wastes prior to final disposal, which has not yet been determined. Treatment will be performed in a new facility to be built adjacent to the silos. The wastes must be retrieved from silos in an efficient and reliable way and delivered to the treatment facility. This proved to be no simple chore, given the condition of the silos and associated constraints. Also, there are approximately 10,000 dry tons of waste in the silos with variable moisture levels, averaging about 30 % by weight (25% to 65% range).

The first challenge of covering the wastes with bentonite has been successfully met. The second phase of retrieving the wastes form the silos is not due for a few years. However, conceptual design and configuration of the retrieval system have been developed as part of the Conceptual Design Report (CDR) prepared by PARSONS to remediate the K-65 wastes. The system is based on the utilization of hydraulic mining techniques, and is based on similar successful applications.

Bentogrout Emplacement

An application demonstration program was developed and carried out by PARSONS to confirm the applicability of the alternative selected by EE/CA and to provide the basis for the full-scale implementation of the removal action concept.

During the demonstration test, the optimum and other applicable mix formulae were developed. Optimum mix was determined based on the slurry physical characteristics, area coverage by flow versus time, setting time, pumping requirements, adhesion, dehydration, and reslurrying characteristics after setting. Based on the results of this demonstration test, design/operational requirements for the full-scale implementation were developed as presented in Table 1.

Table 1. Design/Operational Requirements.

Mix Formulas

Description	Optimum	Intermediate	Heavy
BentoGrout % Weight	25*	30*	40**
Water per 23 kg (50 lbs.) Bentogrout - Liters (Gal.)	68 (18)	53 (14)	34 (9)
Specific Gravity (Slurry)	1.18	1.22	1.31

Batch Values

Description	Optimum	Intermediate	Heavy
Water Liters (Gal.)	668 (176.4)	646 (170.8)	299 (79)
BentoGrout Kilograms (Lbs.)	222 (490)	277 (610)	199 (439)
Batch Volume Liters (Gal.)	757 (200)	757 (200)	378 (100)

Mix Preparation

Optimum & Intermediate Mix Time	0	1	2	3	4	5
Water Addition		3 minutes				
BentoGrout Addition				3 minutes		
Final Mixing						1 minute

Heavy Mix Time	0	1	2	3	4	5
Water Addition	1.5 minutes					
BentoGrout Addition			2.5 minutes			
Final Mixing						1 minute

* Weight percent may vary by ±2.

** Weight percent may vary by -2.

The schematic of the full scale system designed by PARSONS is depicted in Fig 1. The BentoGrout material (a bentonite base material by American Colloid Corp.) was delivered by a pneumatic tanker to a receiving area near the K-65 silos. The dry feed material was pneumatically unloaded from the tanker and transferred into a 2-hr capacity feed bin. BentoGrout was withdrawn from the bin by an inclined screw auger feeder and discharged into a weigh hopper. The predetermined dry BentoGrout batch weight was fed into one of two mixing units. Air vented from the bin through a dust collector to control dust emissions. Similar to the demonstration plan, each mixing unit consisted of one 760-L (200-gal) capacity mix tank equipped with side-mounted high shear-type ribbon blender driven by electric motor. The two mixing units (by ChemGrout Corp.) in parallel were served by a common discharge hopper equipped with one high pressure Moyno transfer pump. The entire mixing unit was mounted on an easily movable skid. From the mixing unit, the BentoGrout slurry was pumped into the silos through a distributor/sprayhead assembly unit suspended from the main basket positioned over the center manway and suspended from a mobile crane boom. The system was designed to produce BentoGrout mixes in 380- and 760-L (100- and 200-gal) batches and distribute the mixes into the silo by the distributor/sprayhead at a continuous rate of 76- and 152-L per minute (20 and 40 gpm) respectively. Continuous operation was achieved by alternating between the two mixing tanks. The system was designed to allow for flushing the entire system with water at the end of daily operations, at shutdown, and/or at job completion.

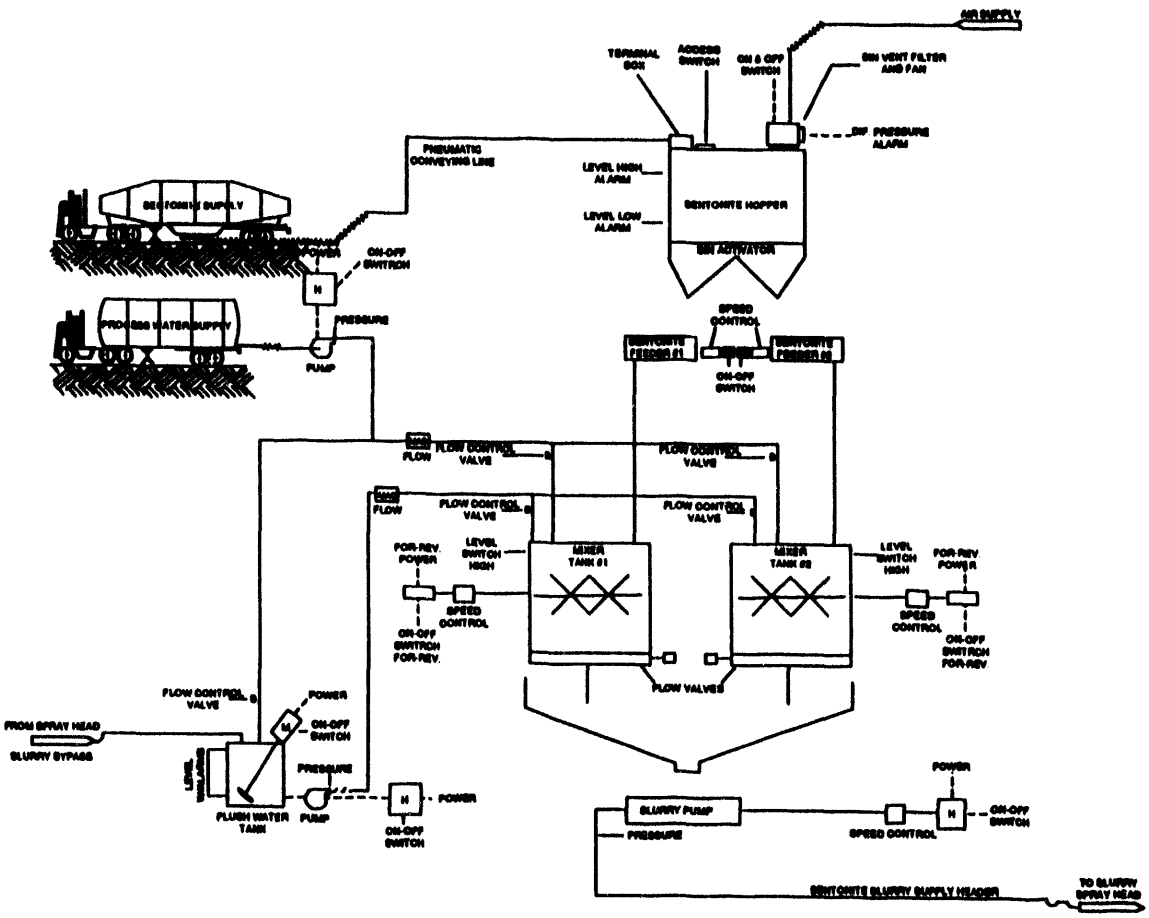

Figure 1. K-65 Soils Bentonite covering system mix and transfer operation

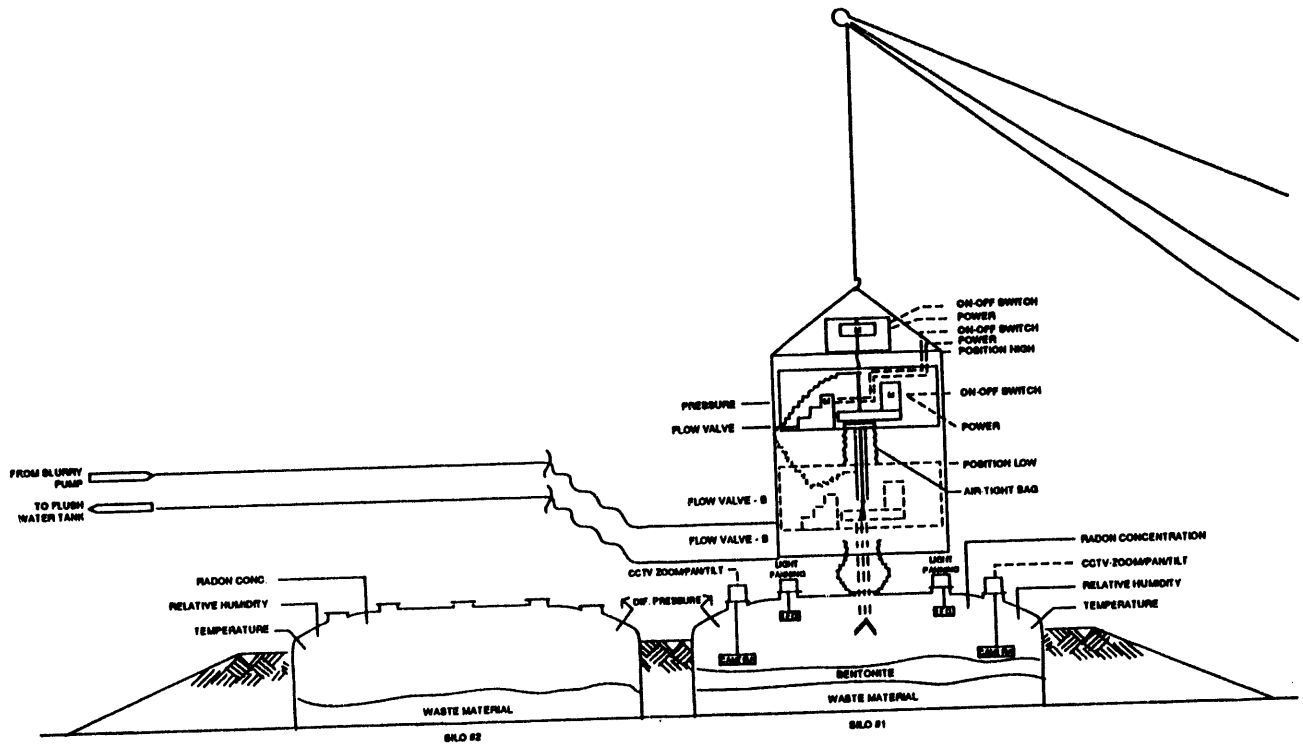

Figure 2. K-65 Soils bentogrout covering system distributor/sprayhead operation

The instrumentation and controls for the BentoGrout covering system, for the most part, were conventional electronic products with very few special devices. Fig 1 and 2 show the types of instrumentation and controls. BentoGrout handling and mixing measurement and controls included level, flow, pressure, speed, and power. The closed circuit television (CCTV) system to monitor the depositing of BentoGrout consisted of two cameras and two lighting bars of four lights each. These were introduced into the silos through the 500 mm peripheral manways. Cameras installed were provided with the capabilities to zoom, pan, and tilt. For the headspace within the domes of the silos, the dynamic measurements included temperature, differential pressure, relative humidity, and radon gas concentration for the purpose of providing logged information to prepare monthly and yearly monitoring reports.

With the exception of the distributor/sprayhead, all components of the system were commercially available. The distributor sprayhead was required to supply and distribute the slurry for even and controlled coverage of the silo contents. No readily-available equipment was found on the market that met the functional requirements. Potential equipment suppliers were contacted, but they could not meet the tight schedule (6 mos) to develop and supply the necessary equipment. Some suppliers proposed extremely complex systems

that would have taken even longer to develop and would have been prohibitively expensive. Now PARSONS was left with only one choice--to design the applicator system. The main criteria that had to be met by the design included:

- Equipment to be lowered into the silos through the center manway (460-mm diameter available opening). The inserted sprayhead must be statically and dynamically balanced. No load is allowed on the silo dome within a restricted, capped center area of 9-m diam. During installation or operation, no live load exceeding 318 kg (700 lbs) is allowed at any point on the dome surface outside of the capped area.

- Sprayhead discharge rate and flow direction must be controlled. The entire surface of the waste in the 24.4 m diameter silo must be covered, preferably from the center manway only. The equipment must have the capability to cover "waste piles" located on the surface under all the manways by properly positioning sprayhead discharge and using intermediate or heavy BentoGrout slurry mixes.

- Design shall accommodate the removal of manway covers from the positioned main basket in an airtight glove bag and shall accommodate the installation and operation of the equipment without permitting radon emissions to the atmosphere.

The distributor/sprayhead assembly is presented in Fig 3 and the installed equipment in operation is shown in Fig 4. The assembly consists of the following main components:

1) The **Quill Assembly** consists of the inner tube (1 in) in a vertical position connected to the slurry feed line at the upper end through a rotating joint. At the lower end, it is connected to the two symmetrically-located distributor arms through a distributor assembly. To ensure that all equipment is dynamically and statically balanced, all rotating parts are symmetrically located. The inner tube is fitted, through the upper and lower sleeve bearings, into a center lift tube designed to be lowered and raised to vertically adjust the position of the arms infinitely through mechanical connectors. The center tube, together with the lift tube, are fitted into the drive tube, which is housed in an 8-1/2 in support tube. The drive tube is supported by ball bearings at the upper and lower ends. The lift tube is equipped with a lift disc at its upper end to accommodate the positioning hydraulic cylinders. The support tube is anchored to the basket weldment floor plate, which supports the entire Quill Assembly.

2) The **Basket Weldment** assembly is a steel frame with welded construction. It is designed to support the quill assembly anchored in the center of the floor plate, the gear motor, the hydraulic cylinders, and the hydraulic power unit. The basket weldment supporting the entire distributor/sprayhead assembly is fitted into a fabricated steel main basket where it is suspended from a chain hoist, and lowered and raised within predetermined limits. Guided movement of the basket weldment is provided by the traveling guides attached to the main basket. In addition, the entire basket assembly was balanced to maintain a true vertical. The drive tube is rotated at 0.5 rpm through a drive train consisting of a gear motor and chain drive.

3) A **Hydraulic Power Unit**, located in the basket weldment, provides motive power to the cylinders for the positioning of the spray arms.

Operation. Prior to the start of operation, the existing radon treatment system (STET) was activated to reduce radioactivity dose to allowable reasonable levels on the dome surface. Air from the silo free board was removed by the RTS at a rate of 1,000 CFM and radon was removed on carbon canisters, then the air was recycled to the silo.

When the system was ready, the main basket containing the installed distributor/sprayhead assembly was

attached to a mobile crane boom. Next, the suspended main basket was carried, then positioned over the center manway of the silo, and securely anchored to the ground. At this time, properly trained and suited operators attached the access ramp and entered the main basket. They connected the slurry supply and flush water lines, as well as electrical and instrumentation cabling. Furthermore, the manway cover was opened and removed in an airtight glove bag provided between the basket weldment assembly and the manway.

After overall system readiness was verified and acknowledged, the distributor/sprayhead was lowered into the silo. Insertion of the equipment was remotely carried out in the control room. The motion was closely monitored by CCTV cameras. Operators remained in the main basket, ready to override operations should that be required. The sprayhead was further lowered to a final position of about 500 millim over the center waste pile. The two spray arms were lifted up from vertical to 75^0 . The sprayhead assembly rotation was started (0.5 rpm) and the operators were instructed to leave the main basket. Instruction was given to start the BentoGrout mix/supply system. Optimum mix (25% wt. solids) was prepared and, with a continuous rate of 152 L/min, was jetted into the silo by the distributor/sprayhead. The entire surface area was covered by spraying the BentoGrout slurry from the two arms on the rotating sprayhead. BentoGrout was applied starting at the silo wall and advancing concentrically toward the center.

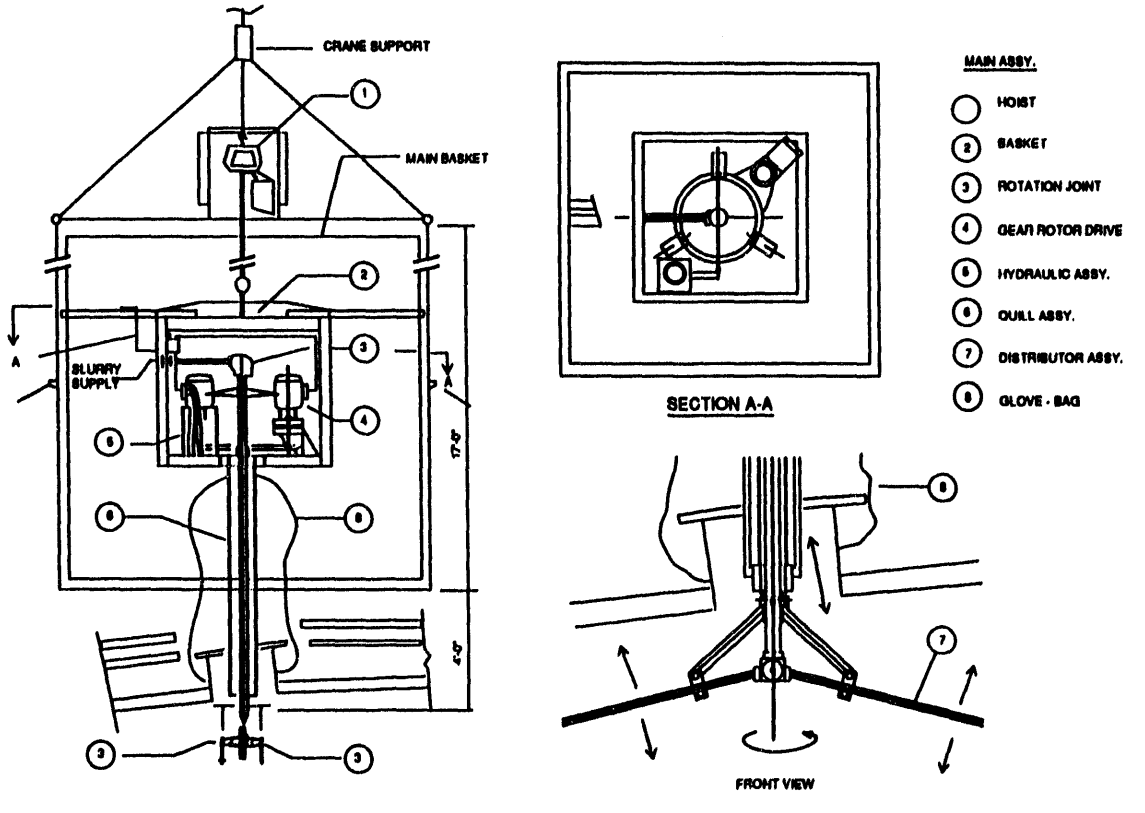

Figure 3. K-65 Soils bentogrout covering system distributor/sprayhead.

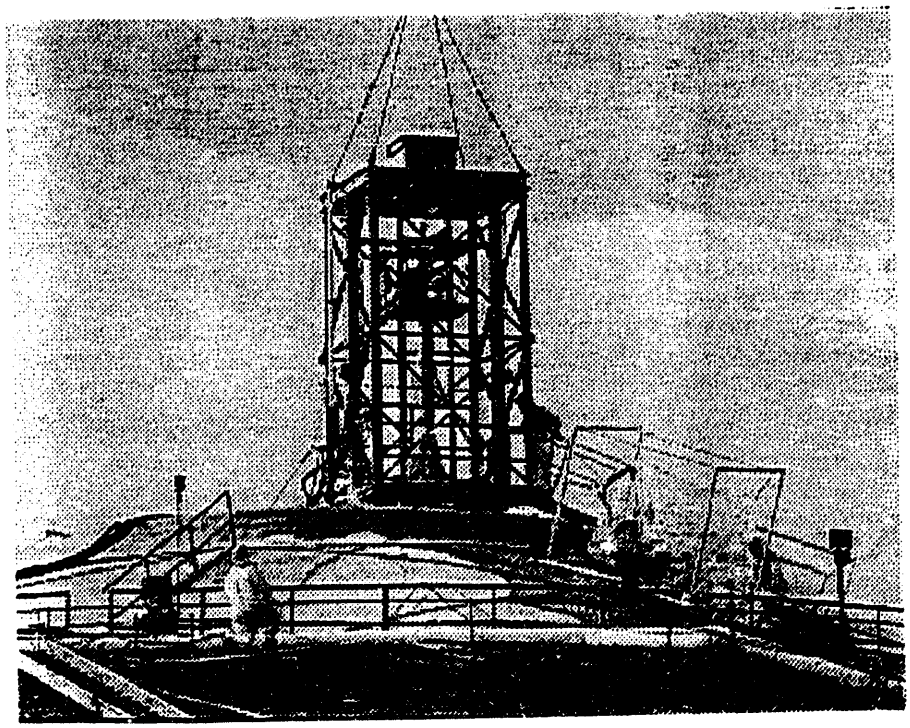

Figure 4.

Coverage was controlled by adjusting the angle of the arms and the height of the sprayhead above the surface and the slurry pressure to the sprayhead. Waste pile coverage was accomplished by applying heavy and intermediate mixes around the pile in layers. BentoGrout was applied in consecutive thin layers until a minimum thickness of 300 mm (1 ft) was achieved at any point. At this time, operation ceased. Lines and sprayheads were flushed and drained. Operators re-entered the main basket. Equipment was removed in reverse order of installation and the center manway cover was replaced in an airtight glove bag. After removing and safely discarding the glove bag, the operators left the main basket and readied it for removal. The main basket was transferred by the crane to its standby position on the ground. Operations were identical for both silos.

Coverage of the surfaces in both silos was completed in one week. Operations were smooth, with a minimum of downtime. The distributor/sprayhead system proved to be highly reliable in fully remote operation.

After emplacement of BentoGrout slurry into Silos 1 and 2, the total waste volume has been increased by 355 and 310 m^3, respectively. The depth of the BentoGrout layer over the residue surface averaged 500 mm in Silo 1 and 670 mm in Silo 2. Radon gas concentration in the silo free board has been reduced from 25 - 30 μCi/L to 45 - 220 nCi/L, resulting in an overall reduction efficiency of 99.8%.

RETRIEVAL OF MIXED WASTES FROM CONFINED SPACES

Slurry Retrieval System

Many of the same constraints on the application of the BentoGrout to cover the silo contents also apply to the retrieval of those contents. The severity of these constraints is more acute in the case of retrieval, as discussed later.

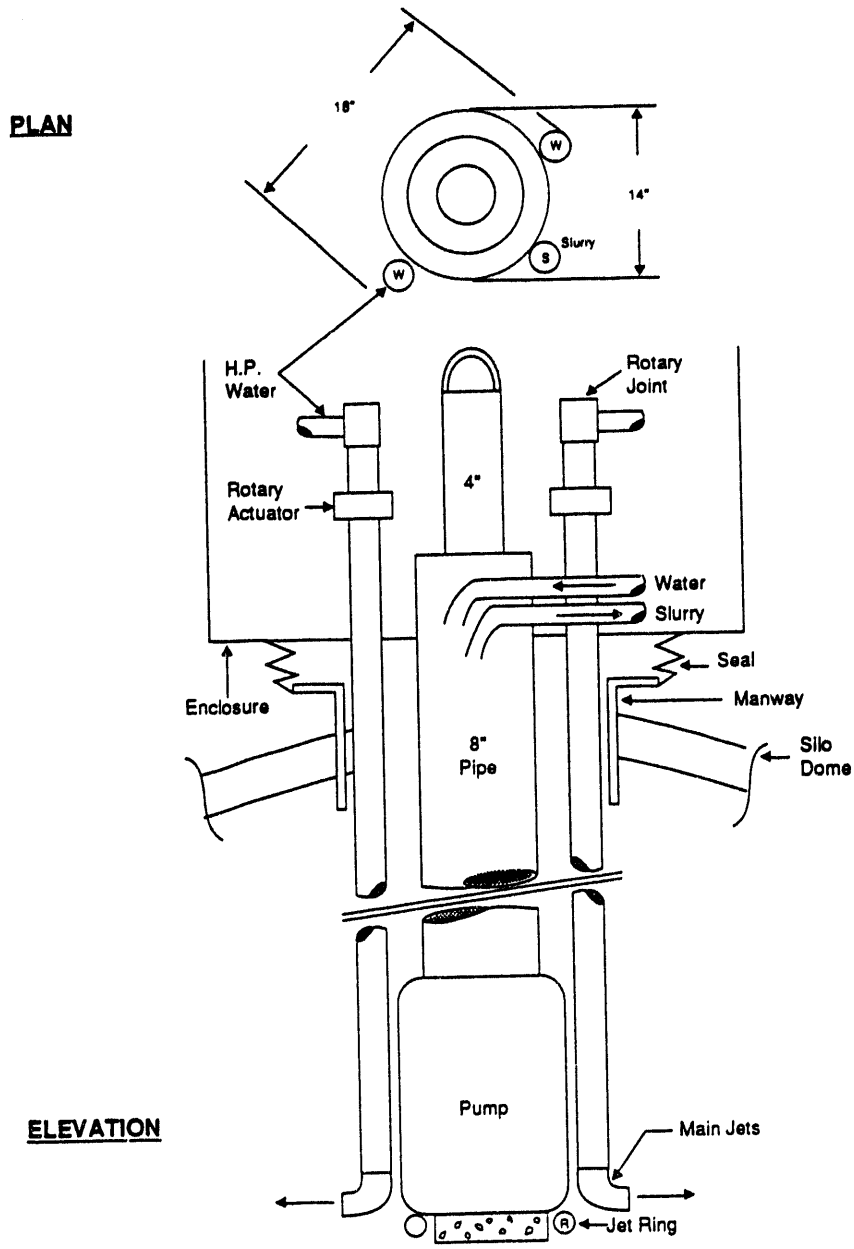

Figure 5. Caisson assembly Functional

An integral part of remediating the Fernald site is the retrieval and treatment of the waste from the silos for stabilization prior to disposal. Several alternates for treatment and final disposal have been considered including vitrification, chemical separation, solidification, shallow burial, and deep geologic disposal. Common to all of these methods is the necessity of retrieval of the waste from the silos. The retrieval action is governed by the following params and/or constraints:

1) Access to silo contents is limited to five manways, 500 mm diameter (inside) each. The vertical projection of the four peripheral manways is equivalent to only 360 mm.

2) The system must be large enough to retrieve 15 t of dry solids/day and must operate without imposing any loads on the silo structure. This requirement is extremely critical since the system operates 24 hr/day, 7 days/week, in all types of weather including high winds, tornadoes, heavy rain, and snow.

3) The system must be capable of mobilizing all the waste in the silo, conveying it outside the silo, and delivering it to the treatment facility. All this must be accomplished without breaching the integrity of the silo radon gas abatement system.

4) Foreign solid materials are present in the silos. These include pipe pieces, wrenches, wire, plastic sheets, cans, bottles, etc. which could have an impact on the method and equipment selected.

5) The system must be remotely operated and automatable. The ability to remove large quantities of waste from a single position (without being moved) is highly desirable. It must also be easy to maintain and decontaminate.

6) The system must be retrievable from the silo in case of failure.

As you can see, it should now be apparent that the retrieval of the silo contents in a safe and reliable way presented a major challenge. Several methods for removing the waste from the silos were considered. These included bucket elevator, auger screw, other mechanical systems, and the slurry method. This paper addresses only the slurry, or hydraulic mining, method.

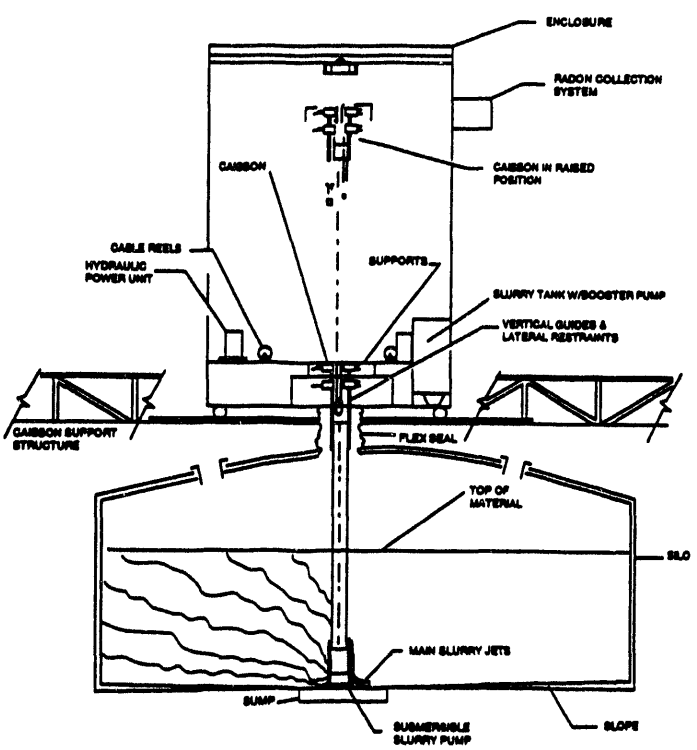

Figure 6. Caisson deployment

Two slurry systems were evaluated. The first one consisted of a slurry pump supported by a cable, two independent and extendable water supply pipes, each with a nozzle at the end, supported from a telescoping pipe for rigidity. This option presented many problems:

1) It could not be reliably automated.

2) Certain modes of failure could make it impossible to retrieve the system from the silo.

3) Frequent movement of the assembly between manways would be required. This would result in prolonged work interruptions and would increase the danger of contact between the assembly and the silo dome, as well as increase the possibility of radon gas escaping to the atmosphere and the probability of worker exposure.

4) The necessity for frequent movement makes the installation less permanent and, therefore, more susceptible to the dangers of inclement weather.

The second slurry system evaluated, and selected, is a specially designed integrated slurry pump/water jets system that we call the "caisson." The caisson meets or exceeds all the constraints and criteria listed above.

The caisson system is based on proven technology and uses commercially available components. The caisson consists of a submersible slurry pump with a jet ring, two oscillating high-pressure water main jets, piping, cables, etc. that are integrated and mounted to a rigid pipe to form a compact and portable assembly.

The slurry pump is a high head, low speed centrifugal type. It was very important to select a pump with the highest ratio of impeller diam to overall outside dimension that would fit through a hole of about 460 mm in diameter. Also, the pump must have a fairly flat performance curve to prevent upset conditions. The pump is driven by an electric motor.

The rigid pipe assembly consists basically of 8-in stainless steel pipe that attaches securely to the top of the pump and extends through the manway when the pump is at the bottom of the silo. To the top of this pipe is welded a length of 4-in stainless steel pipe to complete the caisson support system. This assembly provides the necessary rigidity and support and the ability to position the caisson vertically through the center dome manway. Split sleeves and easily removable roller bushings provide for vertical alignment of the rigid pipe and caisson without contact with the dome or manway. The rigid pipe also provides the conduit and/or support for the slurry and water pipes, hoses, and cables.

The two high-pressure water main jets are installed near the pump suction, 180^0 apart. Each jet is at the end of its own water supply pipe that terminates in a rotary joint and hydraulic actuator outside the silo. The jets are oscillated about 240^0 by the hydraulic actuators. The jet nozzle directs a stream of high pressure water at the consolidated material, at a slight upward angle. The slurried material then flows by gravity towards the pump suction, following the channel created by the jet stream. The angle of the nozzle is a function of the particle size distribution, viscosity, specific gravity, and distance.

The jet ring consists of a pipe ring mounted around the pump suction with small holes (or nozzles) directed in a generally downward direction below the pump. The jet ring is supplied independently from the same high pressure water source as the main jets. The jet ring serves to slurry the material immediately under and around the pump, thus allowing the caisson to sink into the material. Additionally, the jet ring provides water to prevent the pump from starving, when needed, and will be used for slurry density control.

The caisson is designed to retrieve 15 dry tons of K-65 material in 24 hrs, based on a slurry density of 20 % solids by weight. This very conservative approach was selected due to lack of characterization of the K-65 material at this time. However, analyses of the available particle size distribution and historical data

indicate that the K-65 material could be retrieved at much higher slurry densities, which would ease the operational requirements of the caisson.

Installation. The entire caisson system is assembled outside the silo. A specially designed platform is rigidly installed over the silo manway. The caisson assembly is then lowered into the silo through the manway by a mobile crane. Moveable plates and roller guides on the platform are used to prevent any contract between the caisson and the silo dome or manway. The caisson is lowered until it reaches the consolidated material. The water and slurry lines and the electric cables are connected. The system is started (as described later) and the caisson is lowered to the desired position. The caisson is then anchored to the platform above the silo with lateral and vertical supports before becoming fully operational.

Expandable isolation bags will be used and strict procedures will be implemented to capture any radon gas escaping from the silo during deployment and operation of the caisson and to facilitate removal and replacement of the manway cover.

Operation. Once the pump inlet screen reaches the top of the waste material or the BentoGrout, water is supplied to the jet ring. The jet ring directs the water under and around the pump assembly, in a predetermined pattern, so as to slurry the material and allow the caisson to sink by gravity. Once the caisson is down to the desired or predetermined position and anchored in place, the main jets are started. After a slight delay to create a slurry pool, the pump is started. The density of the slurry discharge is then monitored and the flow of water from the jet ring and the main jets is varied until the desired slurry flow and density are achieved. When the system is thus balanced, it is placed in the automatic mode.

The automation system maintains the desired conditions by monitoring and controlling slurry discharge, water pressure, water flow, main jet oscillation speed, and flow through the jet ring. Additional control or fine tuning may be accomplished by varying the pump speed. The system will also record flow rates, pressures, slurry density and speeds that will form the basis for adjustments, if needed.

The caisson system operates fully submerged. It is anticipated that the caisson will be lowered to the bottom of the silo as quickly as possible and left to operate there for very extended periods of time. As the main jets oscillate through overlapping 240^0 arcs, they will slurry the waste around the pump, which discharges the slurry outside the silo. This action creates a cavity into which more material slides and is then slurried. This process continues until all the waste material above the plane of the main jets is removed.

Removal of the waste material remaining below the plane of the main jets will be considered the "cleanup" action. During this stage, accurate control of slurry density becomes difficult and the density could drop substantially. However, what is important at this stage is the removal of the material, not the rate of removal. The cleanup can be accomplished by manipulating the position of the caisson, replacing the main jet nozzles with specially designed "cleanup" nozzles, providing auxiliary lancing at the outer reaches of the silo, or any combination thereof. In all cases, variable or intermittent slurry pump operation may also be required.

The entire system is operated in balance. The water supply is monitored and compared to the slurry discharge. The flow rates are automatically adjusted to minimize the chance of increasing the water content of the waste in silo. Given the fact that the moisture content in the silos presently varies from about 25 % to 65 %, and based on our experience with this type of operation, we believe that the probability of a significant increase in the resident water content of the waste is very small. Water used in the slurry operation is recycled from the treatment facility. Additional water is made up from the process water system. Process water will be used to flush the system for shutdown or maintenance.

It is expected that the vast majority of the silo contents will be retrievable with this system (as a stand-alone from the center manway). Residue characterization may result in a need for auxiliary lancing of the residue along the heel of the silo during the final cleanup. This lancing will be performed with a simple pipe and nozzle arrangement through the peripheral manways without disrupting the operation. The slurried material will flow along the sloping floor of the silo to the low point where the slurry pump is located. If necessary, the pump system could be moved from one manway to another; however, conceptually, it will be located in the center manway. Retrieved waste, in slurry form, will be delivered to the processing facility without any additional handling except, perhaps, a booster pump. The slurried material will be double contained to minimize the possibility of spills, leaks, or contamination of the environment.

Any solid object encountered will simply sink straight down or even be pushed away from the caisson by the action of the main jets. These will remain in the silo to be retrieved later as part of the decontamination and decommissioning operation. However, the waste will be washed from these objects and be discharged by the pump. The impinging of the high pressure water stream on the silo wall will in no way affect the integrity of the silo. However, any loose material on the wall could be scabbled by the jet action and removed with the waste.

The environmental integrity of the silo is maintained through the use of isolation bags and enclosures around the support platform. The entire operation within the silo will be monitored by the CCTV cameras described earlier.

CONCLUSION

There are many sites that have mixed wastes in confined spaces that must be remediated. However, some immediate action may be necessary to minimize environmental impact while awaiting final remediation.

At Fernald, the short-term objective of mitigating radon gas emissions from the K-65 silos to the atmosphere has been successfully met through the application of Bentogrout slurry. We are confident that the other objective of retrieving the wastes from the silos for treatment and disposal will be similarly accomplished using the slurry retrieval system. It is also important to note that relatively simple equipment can be quickly designed and built, based on proven technology and commercially available components, to satisfy sensitive and complex environmental functional requirements.

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CO-DISPOSAL OF MIXED WASTE MATERIALS

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ABSTRACT. Co-disposal of process waste streams with hazardous and radioactive materials in landfills results in large, use-efficiencies waste minimization and considerable cost savings. Wasterock, produced from nuclear and chemical process waste streams, is segregated, treated, tested to ensure regulatory compliance, and then is placed in mixed waste landfills, burial trenches, or existing environmental restoration sites. Large geotechnical unit operations are used to pretreat, stabilize, transport, and emplace wasterock into landfill or equivalent subsurface structures. Prototype system components currently are being developed for demonstration of co-disposal.

INTRODUCTION

Westinghouse Hanford Company, under the direction of the U.S. Department of Energy, Richland Operations Office, is developing systems for co-disposal of waste materials. Co-disposal, as defined here, is the disposal of radioactive and/or hazardous process generated waste materials in combination with contaminated waste materials produced from waste management and environmental restoration retrieval actions. Co-disposal is a significant waste minimization and resource-use avoidance technology. Development testing and demonstration activities are being conducted consistant with a requirement of (1) National Environmental Policy Act-approved, geotechnical test-bed located at the Hanford Site, Richland, Washington. The co-disposal process is being implemented at an environmental restoration location wherein waste materials are exhumed, treated, and replaced in the geologic media at the location. The process can be implemented optionally where waste materials are exhumed from an environmental restoration location, treated, transported, and placed in a landfill or similar subsurface waste disposal location. Onsite treatment and disposal will be conducted at past-practice Resource Conservation and Recovery Act of 1976- (RCRA) (2) or Comprehensive Environmental Response, Compensation and Liability Act of 1980- (CERCLA) (3) contaminated industrial waste trench or landfill locations.

The benefits of co-disposal are many and, by using these co-disposal technologies for mixed waste landfills, significant efficiencies and cost savings can be realized. Co-disposal utilizes 100 % of the volume of a landfill by incorporating packaged mixed waste into a matrix of treated waste feed materials originating from multiple waste-producing processes. This high-durability, high-leach-resistent, high-strength and low-conductivity material is called "wasterock."

Treated feed materials (i.e., wasterock) can significantly reduce radiation dose by providing shielding during waste package placement and subsequent landfill operations. Wasterock will provide secondary confinement of packaged waste and physical stability to the landfill. Inefficient and costly backfilling of the landfill with uncontaminated materials is eliminated. Co-disposal will reduce regulatory restrictions on barrier design of landfills. Waste package disposal can be increased by more than 300 % if a mixed waste landfill and co-disposed interstitial package wasterock is used. This increased efficiency for a typical RCRA mixed waste landfill can translate to a cost savings of greater than $100,000,000 per landfill.

Demonstration of the co-disposal process and geotechnical equipment is planned in conjunction with a soil-wash treatability study of uranium and polychlorinated-biphenyl-contaminated soil materials. The demonstration will use soil-washing sludge, contaminated-liquid chemical process evaporator condensate, and coal-fired power plant fly and bottom ash as wastestream feed makeup materials. Both polymer and cement treated wasteforms will be produced.

PROCESS FEED CONTAMINATED MATERIALS

The essence of co-disposal is the incorporation and transformation of materials that would otherwise be considered waste into a useful feed material for underground stabilization and isolation of mixed waste landfills or other similar waste disposal structures (4). Extremely large volumes of these waste materials have been and will continue to be generated at the Hanford Site and other waste management sites (government and private sector) over the next few decades. These materials can originate in the form of bulk or packaged liquids, solids, or slurries. Typical Hanford Site-generated materials are discussed as examples.

Mixed fission products, activation products, transuranics, heavy metals, and organic solvents, etc. have contaminated large volumes of geologic media (soil materials) through surface and subsurface structures. These include landfills, trenches, ponds, cribs, reverse wells, and similar underground structures. These materials can be retrieved and transported to areas on the Hanford Site that are more environmentally acceptable and less accessible to the public. A significant portion of these materials will require treatment as defined by regulatory review and approval.

Similar contaminants are often included in the matrix of retired chemical separations plants, reactor buildings, and auxiliary buildings. As structures are decontaminated and decommissioned, a large volume of contaminated rubble will be generated. The contaminated fraction of this rubble may require treatment and/or transportation to a more suitable and approved disposal location.

Structures such as chemical separations plants, evaporators, and waste treatment plants produce large quantities of low-level radioactive and trace-quantity contaminated hazardous materials liquids. These liquids have been discharged to ponds, evaporation basins, infiltration cribs, and similar waste disposal structures. Several wasterock formulations can use these liquid waste materials. Regulatory approval of beneficial use of these liquids is highly probable.

Ash originating as a byproduct of coal-fired steam generation plants at the Hanford Site has been produced in large volumes during the past 5 decades. This material (fly ash, bottom ash, and aggregate) is a solid waste and requires expensive disposal. Most of the ash currently is stored in large above- and below-grade piles. Ash can serve as a filler/binder agent in most wasterock formulations. The ash has been chemically analyzed and found to be within regulatory limits for wasterock.

Retrieval of contaminated solid waste and associated geologic media during site characterization and sampling operations produces significant quantities of bulk contaminants and well cuttings. These are typically placed in steel drums. Operational cleanup and spill spoil materials are typically collected in the same containers. Drummed waste, especially mixed waste, requires transport and acceptance by an onsite permitted treatment, storage, and disposal facility. This is an expensive activity, involving increasing economic and environmental liabilities. This waste could serve as an aggregate for most wasterock formulations and could be used before storage requirements are prompted.

ADMIX FEED MATERIALS

Polymers can be added to contaminated soil and aggregate materials to form a thermoset-injectant slurry, which in turn forms a stable leach-resistant monolith. Polymers can be added to the equivalent contaminated materials and can be cast into large blocks. These can be used at the site of contaminant excavation, or they can be transported to a disposal landfill. The contaminated aggregate is mixed with a monomer that is reacted with a binder to form a durable solid after appropriate cure. These include polyacrylic acids, methacrylates, and styrenes (5).

Concrete formulations consisting of contaminated soil and aggregate utilizing cement and pozzolana as binders is a typical, cost-effective stabilization material for mixed wastes. Other concrete formulations (e.g., sulfur concrete) are derived from contaminated soils, aggregate, and a thermoplastic cement (modified sulfur cement, polyethylene). This material requires homogenization and heating of the particulate and binder. These formulations also can be used as previously discussed (onsite), or they can be transported to a distant disposal location for final disposal.

Where there is a concern with leachability of specific radionuclides or hazardous elements, either in wasterock or in waste containers within the wasterock matrix, sequestering agents can be added to treated slurry materials. Several tests have been conducted to evaluate the effectiveness of zeolites, naturally occurring phosphates, naturally occurring pyrrotite, ferrous sulfide, anion exchange resins, and mixed metal oxide/hydroxides (6). These or other agents can be added to wasterock before cure to inhibit transport of contaminants into the geologic media surrounding the waste disposal landfill, trench, etc. These materials induce precipitation, ion exchange, molecular sieve entrapment, chelation, or other mechanisms that retard contaminant transport to diffusion-controlled rates that are within regulatory limits.

WASTEFORM QUALIFICATION

Wasterock formulations will be qualified for each combination of waste and admix materials. Qualification is a formal process whereby wasterock is tested against several prescribed protocols. Current prequalification activities primarily follow American Nuclear Society procedure 16.1 (7) and the U.S. Environmental Protection Agency Toxic Characteristics Leaching Procedure for hazardous material and radionuclide leach resistance. American Society for Testing and Material and American Petroleum Institute standard tests are used for strength, durability, and flux density.

Formulations are prequalified for use in solidification processing. Qualification verification is completed as part of quality control conducted concurrent to process operation and subsequent destructive testing. Qualification tests depend on the type of waste used in the wasterock formulation, i.e., solid, hazardous, or mixed radioactive and hazardous.

MOBILE FIELD UNIT OPERATIONS

The co-disposal operational system is based on several transportable and mobile unit operations. These unit operations or modules can operate as individual subsystem components or in combination with other components, dependant on application of retrieved or generated waste materials or an holistic system. Solidification treatment, thermal treatment, admix treatment and other geotechnical and geochemical processes may be used alternatively. The primary unit operations currently used for co-disposal are delineated in the following operational description.

Transport, Mixing, Shearing, and Pumping Module

This semi-truck trailer-mounted module carries both liquid and dry (granular or powder) nonhazardous and nonradioactive feed materials in tanks and bins of 3.5 m^3 and 1.8 x 10^1 m^3, respectively. Dry feed materials are fluidized in separate bins with purified nitrogen gas to promote materials handling and metering. Liquid and dry feed materials are metered through pumps and augers into a colloidal mixer by programmable electronics components permitting batch or continuous batch mixing.

Slurry produced in the colloidal mixer is recirculated continuously by a shearing pump that ensures that the materials are wetted and hydrated. Slurry is then transferred to a pumping tank and alternatively pumped to the next unit operation by either of two progressive cavity pumps or a large dual-action piston pump. This variability in pumping capacity permits required variability in low- or high-pressure and low- or high-volume throughputs requirements. Maximum capacity throughput for progressive cavity pumps is 4.4 x 10^{-3} and 2.6 x 10^{-3} m^3 s^{-1} and for the piston pump at pressures of 5.3 x 10^{-3} and 2.5 x 10^2 kgm^{-2}, respectively.

The unit operation components are powered by a 1.7 x 10^5 w diesel power plant that provides hydraulic, pneumatic, and electrical power to component as required. This unit operates as a stand-alone unit, or the unit can operate tethered or interfaced to other units through slurry transfer piping.

Batch Plant/Silos Module

A mobile, semi-truck multitrailer-mounted unit operation for contaminated and noncontaminated materials processing is used either at the point of waste retrieval or at the point of landfill/trench placement. This module is capable of either wet or dry batch operations. In addition, the module can be operated at ambient temperatures for typical slurry materials production or at elevated temperatures for production of, for example, modified sulfur-cement materials.

The module has a throughput of 5.0 x 10^{-1} m^3 s^{-1}. Materials are introduced to the module through two silos. The primary silo is a two-compartment arrangement with a combined capacity of 58.3 m^3. The secondary silo or single compartment aggregate bin has a 38.2-m^3 capacity. Metering and mixing is operated via a load-cell-based 9.2-m^3 recirculating screw batcher. Batch formulation control is operated by a programmable electronic subassembly. Dry particulate amazons (dust control) are collected and recycled into the module using a large, high-throughput roughing filter and high-efficiency particulate air filter components.

The module is electrically powered from a mobile auxiliary feed 8.0 x 10^4 w electrical generator. The use and configuration of this module is highly variable, dependant primarily on the wasterock formulation being used.

Materials Classification and Separation Modules

Bulk dry feed materials often require pretreatment to obtain optimum or process-acceptable materials. Standard bulk loading, classification, and conveying modules are modified for use under hazardous and radiation health physics conditions. Primary materials separation for both uncontaminated and contaminated feed includes grisleys, vibratory screens, and large dry-feed hoppers. Secondary materials handling and separation involves shaker classifiers and screens coupled to conveyors (mechanical and pneumatic). Separated materials, either contaminated solids or clean feed stock, are stored in hoppers before being processed.

Materials classification and separation modules are primarily interfaced with batch plant components after waste from slurry formulation. However, the same modules can be used as pretreatment unit operations at the point of contaminated materials retrieval.

Chassis-Mounted Pump and Boom with End Effectors

This fully mobile module carries a large-capacity pump, boom, and end effectors (remote-operated tools used on the terminating portion of the boom) used for materials placement. The primary use of this module is for the backfilling of existing mixed waste landfills. Throughput of the module at maximum capacity is 3.2×10^{-2} m^3 s^{-1} using a dual-action piston pump. Slurry from the pump is transferred through a four-part roll-and-fold boom. The boom is fully articulated and capable of vertical, lateral or subgrade reach of approximately 32 m. The sluing radius of the boom is 6.3 radians. The boom reach is required for slurry placement within a landfill with a protracted placing distance. The boom also allows placement of slurry within a landfill where radiation dose is excess of contact handling limits. Slurry placement can be performed through a termination tube affixed to the boom or through a remote, hydraulically operated end effector that uses a coaxial pneumatic placement injector.

The module is chassis mounted and powered by a 2.6×10^5 w diesel power plant with power-take-off drive. All components are operated with hydraulics. This module is a stand-alone unit; however, it can be remotely operated by electronic tethers, thereby reducing radiation dose.

Pressure Injection

Slurry is injected into existing high void-volume underground waste tanks, drainfields, large industrial containers, etc. using this module. The module is modified from its original configuration as a hydraulic jet grouting system. The injector consists of a counter rotating percussion/abrasion subassembly that is interchangeable with tricone drilling bits, a high-pressure cutting tool, a swivel, and nonreturn valves. This subassembly is operated from a 4.2-m-long articulated mast and winch assembly.

This chassis-mounted self-propelled module is powered by a 6.6 kW diesel power plant. All assemblies are powered hydraulically. The module is trammed on independent oscillated crawler tracks for stability and placing site access. The pressure injection module is used independently when in drilling mode and in series with the transport, mixing, shearing, and pumping module during slurry materials placement (injection). Throughput is not limiting.

This unit may additionally be used in its more traditional application of construction of barriers around waste retrieval areas or waste disposal landfill structures. These barriers can be constructed of numerous formulations of wasterock.

Testing and Quality Control Laboratory

In addition to geotechnical equipment unit operations, a mobile laboratory module is used as an integral part of co-disposal. Real-time materials and process testing is conducted in this laboratory. Materials and operations quality-control verification is also conducted using standard procedural testing in this module.

Numerous tests and quality control procedures may be used during materials processing and placement. Present typical laboratory testing involves a spectrum of internationally accepted procedures. Flow-cone testing is done to determine the consistency of slurries and, indirectly, to determine changes in gel or set time. Viscosity (dynamic/kinematic) tests are conducted to determine much the same characteristics as flow-cone measurements. In addition, viscosity measurements are conducted on liquid-feed wastestreams to determine required changes in wasterock formulation composition. Density of the slurry and solid waste stream materials is measured primarily to determine consistency.

Slump is measured on slurry materials to evaluate the consistency and flowability of slurry during placement. Time of set is also used for analysis of placement requirements. Additionally, set time is an important slurry characteristic required for materials hauling and transport time. Phase separation is also

determined to verify regulatory requirements of negligible free liquids used in landfill disposal. Adiabatic temperature change and placing temperature determinations are also important characteristics that require measurement to evaluate materials cure and ultimate strength.

Preparation of samples for long-term laboratory verification testing is also completed in the mobile laboratory module. These verification tests ensure wasterock strength, durability, liquid/air flux density, leach resistance, and regulatory compliance. As a precursor to verification testing, standard laboratory testing of numerous other feed materials are typically completed with the results used as feedback to process control.

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LOW-LEVEL RADIOACTIVE MIXED WASTE DISPOSAL FACILITY - PERMANENT DISPOSAL

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ABSTRACT. The Resource Conservation and Recovery Act of 1976 (RCRA) has specific criteria that must be met when designing, constructing, and operating a land disposal facility for hazardous waste. Radioactive Mixed Waste (RMW) is a hazardous waste that is radioactively contaminated. Westinghouse Hanford Company, in Richland, Washington, is in the process of completing a RMW land disposal facility, which is based on the best available technology compliant with RCRA. When completed, this facility will provide permanent disposal of solid RMW. This paper provides details about the design and permitting process of a RMW land disposal facility to be built in the near future in Richland, Washington for the U.S. Department of Energy. The Washington Department of Ecology has been delegated the authority to enforce RCRA in Washington. The project will provide a Washington Department of Ecology Permitted Disposal facility that will include a double geosynthetic liner a leachate collection and removal system. The admix liners, along with the two high density polyethylene liners and the leachate collection and removal system, provide a more that conservative, physical containment of any potential radioactive and/or hazardous contamination. This disposal facility will be safely designed, constructed and operated to protect human health and the environment from any hazards posed by solid low level radioactive mixed wastes.

INTRODUCTION

Various types of waste have been generated during the 50-year history of the Hanford Site. Regulatory changes in the last 20 years have provided the emphasis for better management of these wastes. Interpretations of the Atomic Energy Act of 1954 (13), the Resource Conservation and Recovery Act (RCRA) (1), and the Hazardous and Solid Waste Amendments of 1984 (HSWA)(2) have led to the definition for solid RMW. The radioactive and hazardous properties of these waste have resulted in the initiation of special projects for the management of these wastes. Other solid wastes at the Hanford Site include low-level wastes, transuranic, and nonradioactive hazardous wastes.

The RMW disposal at U.S. Department of Energy (DOE) facilities is subject to the RCRA (1) and HSWA (2). The U.S. Environmental Protection Agency (EPA) granted waste generators and owners/operators of hazardous waste treatment, storage, and disposal (TSD) facilities a national capacity variance for RMW as outlined in Appendix VII of 40 CFR 268 (3), where treatment standards are not well known or defined. Wastes within the national capacity variance were unrestricted from land disposal. The national capacity variance for RMW expired on May 8, 1992. Some case-by-case extensions are pending, but eventually all RMW will be restricted from land disposal.

The HSWA of 1984, identifies minimum waste disposal criteria, known as the "Land Disposal Restrictions" (40 CFR 268) (3), that must be met before disposing of solid waste in a landfill.

In Washington State, the disposal criteria for RMW are very strict. Currently, a few RMWs meet the disposal criteria; therefore, these waste must be stored until treatment is available to condition the waste

for disposal. At the Hanford Site, in south-central Washington State, the Central Waste Complex (CWC) is designed to provide interim and long-term storage of RMW (refer to Figure 1). When completed, the CWC will have the capacity to store more than 75,000 208-L (55-gal) drums of solid waste.

The Westinghouse Hanford Company (WHC) has completed the design of a radioactive mixed waste land disposal facility, which is based on the best available technology compliant with RCRA; 40 CFR 260-265 (4-9) and WAC 173-303 (10). When completed, this facility will provide permanent disposal of solid RMW, after treatment, in accordance with the Land Disposal Restrictions. The facility includes a double clay and geosynthetic liner with a leachate collection system to minimize potential leakage of radioactive or hazardous constituents from the landfill. The clay liners will be capable of achieving a permeability of less than 1×10^{-7} cm/s.

To obtain an operating permit for a facility of this type, as required in 40 CFR 270 (11) and WAC 173-303 (10), is not a simple task. A specific Construction Quality Assurance (CQA) Plan must be developed for the construction of this type of landfill. Guidance for Quality Assurance during the construction is outlined in Technical Guidance Document, Construction Quality Assurance for Hazardous Waste Land Disposal Facilities (12). The CQA Plan is analogous to an inspection plan used during construction. The plan identifies appropriate documentation to ensure regulators that the facility is constructed to applicable design criteria, plans, and specifications. The plan requires that deficiencies encountered are corrected before construction is complete. It is for this reason that the CQA Plan is such an important part in obtaining a Part A and B operating permit.

The DOE/WHC plans to build a landfill for the permanent disposal of solid radioactive waste in compliance with regulations.

THE SOLID WASTE MISSION

The Hanford Site mission is to transform the Site into the nation's model for excellence in environmental management. This mission will include demonstrating and applying advanced technologies for the restoration of land and the creation of facilities for other productive uses. The Hanford Site solid waste mission is to safely construct and operate the solid waste TSD facilities designed to protect human health and the environment. A disposal facility of interest, designed to protect human health and the environment, is a regulatory compliant landfill. This paper concentrates on details about the design, construction, and permitting of such a facility.

WASTE TYPES

DOE Order 5820.2A (14) defines the types of radioactive wastes. Without regard to source or form, waste contaminated with alpha-emitting transuranium radionuclides with half-lives greater than 20 years and concentrations greater than 100 nCi/g (3,700 Bq/g), at the time of assay, is considered transuranic. High-level waste is the highly radioactive waste material that results from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid waste derived from the liquid that contains a combination of transuranic waste and fission products in concentrations requiring permanent isolation. As defined by DOE Order 5820.2A (14), waste that contains radioactivity and is not classified as high-level waste, transuranic waste, spent nuclear fuel, or byproduct material is considered low level. Test specimens of fissionable material irradiated for research and development only, and not for the production of power or plutonium, may be classified as low-level waste, providing the concentration of transuranic isotopes are less than 100 nCi/g(3,700 Bq/g) (15). This paper discusses a method for the permanent disposal of solid low-level mixed waste.

The EPA has delegated its authority under RCRA, thus allowing individual states to manage hazardous waste programs. Washington State hazardous waste regulations are codified in the Washington Administrative Code (WAC), "Dangerous Waste Regulations" (10). Washington State regulations are more restrictive than the Federal RCRA regulations and cause many additional wastes to be regulated. These wastes are called dangerous wastes in Washington State.

PAST PRACTICES

Hanford Site contractors have buried radioactive solid waste directly into shallow land disposal since 1944. Waste from reactor operations, chemical processing and separations, research and development activities, and other DOE programs have been disposed. Contamination in these wastes consists of fission products, induced activation products, and transuranic isotopes. Solid wastes originate from both onsite and offsite generators. Currently, wastes are segregated by waste type and handled according to the regulatory criteria governing each waste type. Because it is no longer allowable to dispose of RMW in this manner, Subtitle C (RCRA 1976, Section 3004, paragraph o) of RCRA requires minimum standards for disposal facilities and surface impoundments. Disposal facilities, in accordance with Subtitle C, will be built at the Hanford Site for the disposal of solid low-level RMW.

FUTURE APPROACHES

Figure 1 depicts solid waste management in the year 2000 at the Hanford Site. There are numerous planned facilities for the TSD of solid wastes. The goal of these TSD facilities is to provide safe, efficient, and regulatory-compliant management of solid wastes. Based on RCRA regulations, all hazardous waste must either be treated by a specified technology or meet strict concentration limits before being disposed in a RCRA-compliant landfill. Currently, the Hanford Site stores wastes (Fig. 1) until treatment and disposal units are available. A Performance Assessment (PA), in accordance with DOE Order 5820.2A (14), is driving the Hanford Site to severely restrict the use of shallow direct burial trenches.

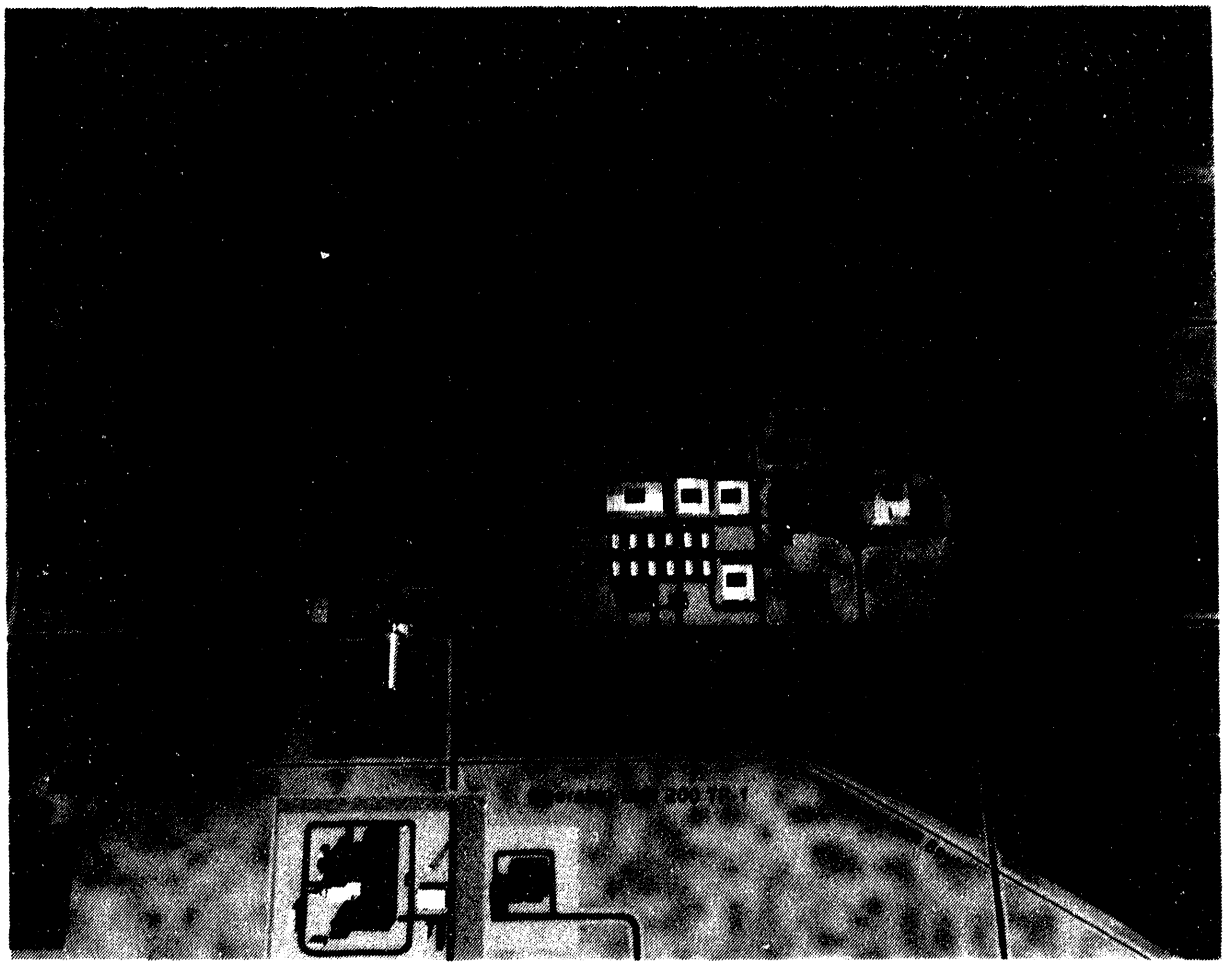
Existing trenches at the Hanford facility do not meet RCRA leachate collection standards. Once the PA is complete, low-level waste disposal will be restricted further. Barriers similar to RCRA liners may be used in disposal sites for disposal of longer-lived radionuclides.

RADIOACTIVE MIXED WASTE DISPOSAL CAPACITY

Currently, permitted RMW disposal capacity does not exist on the Hanford Site. Because national RMW disposal capacity is also limited, it is appropriate that a RCRA-compliant landfill be constructed at the Hanford Site. Onsite disposal capacity further eliminates the risk and expense of offsite transport of regulated wastes across public access transport corridors.

MIXED WASTE LANDFILL

The purpose of the mixed waste land disposal facility is to provide disposal capacity on the Hanford Site for solid RMW. Figure 2 provides a conceptual picture of the landfill. The landfill is designed to handle both contact-handled (surface dose rate $\leq$ 200 mrem/h) and remote-handled (surface dose rate $>$ 200 mrem/h) waste. The landfill will be limited to constraints developed as part of a PA modeling effort. The PA will determine the upper bound for the allowable concentration (activity-Bq/Volume-m^3 or Ci/Volume-ft^3) of radionuclides in the waste for shallow landfill disposal. This means that the landfill will have upper limits for a given concentration of a specific radionuclide based on the PA effort. The RMW



Project W-272 (Capital Work Order)
- A1 Special Case Waste Storage Facility

Project W-026 (Expense Funded)
- O B1 Radioactive Mixed Waste Disposal Facility (218-W-5/T31)

Project W-026 (91 LI)
- C1 Waste Receiving and Processing (WRAP) Module 1

Project W-100 (94 LI)
- \+ D1 WRAP Module 2A

Project W-112 (94 LI)
- \+ E1 Long-Term Drum Storage
- \+ E2 Ignitable Drum Storage
- \+ E3 Box Storage
- \+ E4 Transfer Corridor
- \+ E5 Shipping and Receiving
- \+ E6 Automated Stacker Retriever System (AS/RS)
- \+ E7 Hanford Central Waste Support Complex
- \+ E8 Railroad Extension
- \+ E9 North Perimeter Gate, Guard Station and Road to Route 11-A (not depicted)
- \+ E10 Infrastructure (not depicted)

Project W-113 (94 LI)
- O+ F1 Solid Waste Retrieval Facility (218-W-4C/T34)
- \+ F2 NDE/NDA Building

Project W-156 (97 LI)
- O G1 Alpha Caisson Retrieval

Project W-174 (TBD)
- O H1 Enhanced Solid Low-Level Radioactive and Mixed Waste Disposal (not sited)

Project W-219 (Expense Funded)
- I1 Temporary Office and Change Rooms

Project W-221 (97 LI)
- O J1 Solid Waste Retrieval Phase II

Project W-241 (Minor Project)
- K1 Tempory Sodium Storage Units

Project W-242 (97 LI)
- L1 Thermal Treatment Facility

Project W-247 (97 LI)
- M1 Waste Reduction and Recalmation Facility

Project W-255 (97 LI)
- N1 WRAP Module 2B

Project W-312 (94 GPP)
- O1 Mixed Waste Storage

Existing Facilities
- P1 272 WA
- ☐ P2 2401-W PCB and Mixed Waste Storage
- ☐ P3 Low Rads-Front Mixed Waste Storage Units
- ☐ P4 Radioactive Mixed Waste (RMW) Storage Buildings (2402-W series)
- P5 213-W Compactor Building
- ☐ P6 Mixed Waste Storage Phase I (W-240 W Series)
- P7 2 Plant Operations (Non-solid Waste Facilities)

LI = Line Item
GPP = General Plant Project
TBD = To Be Determined

LLBG = Low Level Burial Ground
CWC = Central Waste Complex
SWOC = Solid Waste Operations Complex
Complex Phase I MFA

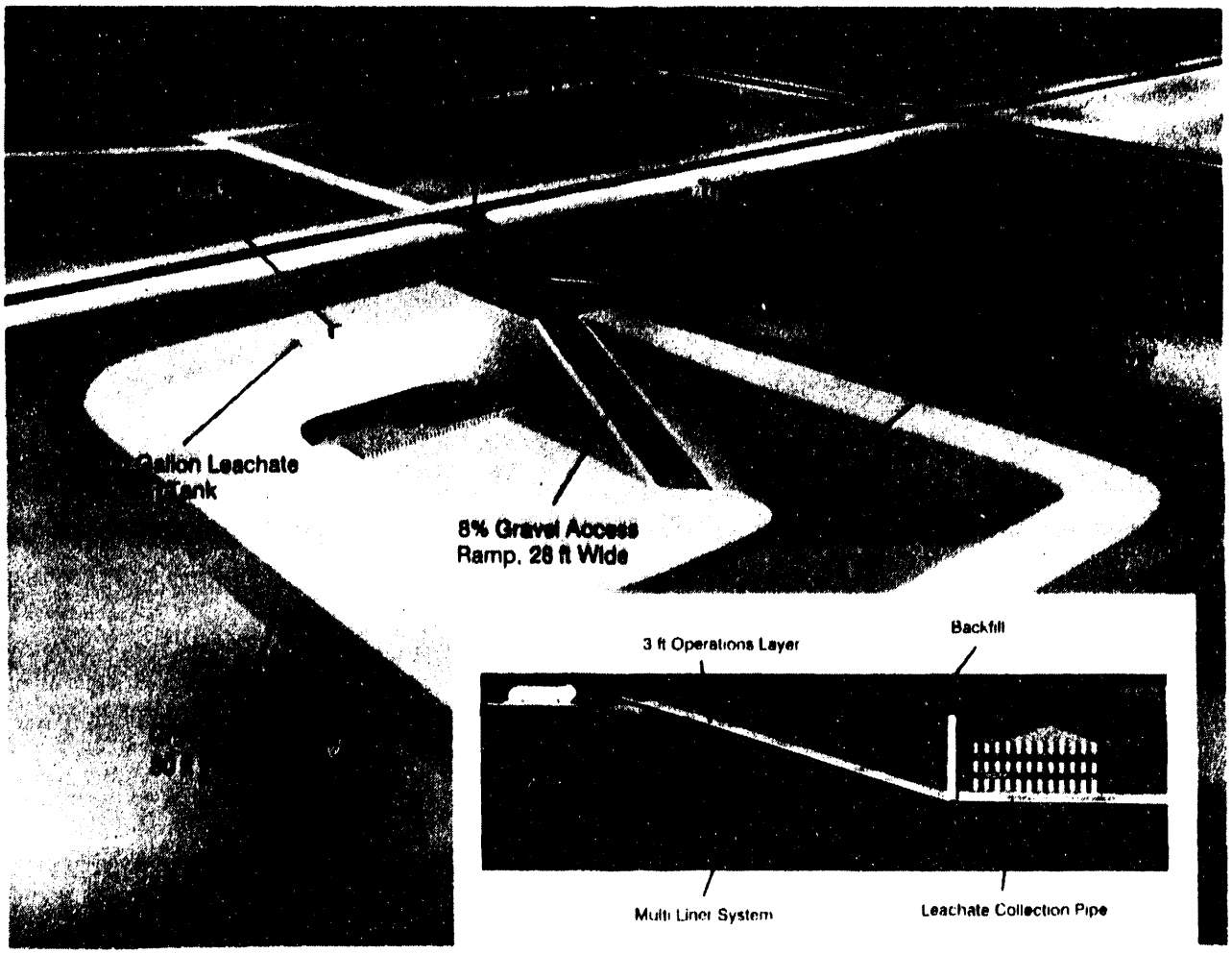


Figure 2. Conceptual layout of the Radioactive Mixed Waste Land Disposal Facility - Non-Drag-Off.

landfill is designed to meet all applicable State, Federal, and local regulations (4-10). The landfill is designed to contain the waste as well as prevent leachate from reaching the environment. Excavation of the landfill will be approximately 68,045 m^3 (89,000 yd^3). The footprint at subgrade is approximately 1.32 hectare (3.27 acres), and at the floor it is approximately 0.23 hectare (0.57 acres) or 76 by 30 m (250 by 100 ft). The excavated depth to subgrade will range from approximately 10.4 m (34 ft) at the west end of the floor to about 11.3 m (37 ft) at the east end. The depth varies so that any potential leachate will be collected at one end of the facility known as the sump collection well. Control of leachate infiltration is achieved by a multilayer liner system consisting of a soil-bentonite mixture (admix with 11 to 14% sodium bentonite), geosynthetic liner materials, and a leachate collection and removal system.

The actual waste volume capacity of the landfill is dependent on the design of cover and its slope. Assuming the base case (waste filled to the surface), the estimated waste volume capacity is 7,646 m^3 (270,000 ft^3) or 37,000 208-L (55-gal) drum equivalents. The operating life of the facility is estimated to be 20 years. However, if under the CERCLA cleanup, new mixed waste sources are identified, current volume estimates will increase substantially and the operating life of this facility will decrease.

Multilayer Liner System

The liner system provides a physical containment barrier between the waste packages and the environment. The liner system is designed to protect human health and the environment from potential leachate that may be generated, if any of the drums were to breach. The multilayer liner system from bottom to top is shown in Fig. 3 and consists of 0.95 m (3.1 ft) of admix (soil mixed with sodium bentonite, with a permeability of 1 x 10^{-7} cm/s or less), 60 mil (1.52 mm) flexible membrane liner (HDPE), 198 mil (5.03 mm) geonet, 185 mil(4.7 mm) geotextile, 0.61 m (2 ft) of drainage gravel, 185 mil (4.7 mm) geotextile, 0.46 m (1.5 ft) additional admix (on the floor only), another 60 mil (1.52 mm) flexible membrane liner, 198 mil (5.03 mm) geonet, a 95 mil (2.41 mm) geotextile, 0.31 m (1 ft) of drainage gravel, 95 mil (2.41 mm) geotextile, and 0.91 m (3 ft) of operational backfill soil.

Note that drainage gravel is not used on the side slopes. A geocomposite acts in place of the drainage gravel. Geocomposites consist of a geonet with a layer of geotextile thermally bonded to each side of the geonet. Geotextiles perform the following functions: separation, filtration, and cushioning. Geonets provide a redundant drainage system in combination with the drainage gravel. Transmissivity, for a synthetic drainage layer (EPA requires greater than 5.4 x 10^{-4} m^2/s or 0.0581 ft^2/s), is the primary selection criteria for geonets. The flexible membrane liners, in conjunction with the admix, provide a physical containment barrier of potential leachate to the environment.

On the side slopes of the landfill, the flexible membrane liner is textured on both sides (Type I HDPE) to mitigate sliding between the liners and the subgrade (slope failure). Generally, a factor of safety of 1.5 for static conditions and 1.1 for dynamic conditions are considered adequate for a facility of this type and the minimum acceptable values for the design analyses. Factors of safety can be calculated using the Infinite Side Slope equation (Stability Analysis of Earth Slopes, (17):

$$FS = \frac{(c/\delta d)\sec\alpha + [(1-r_u)\cos\alpha - c_s\sin\alpha]\tan\phi}{[\sin\alpha + c_s\cos\alpha]} \qquad (1)$$

where:

FS = Factor of Safety
c = Effective Cohesion, kg/m^2 (lb/ft^2); zero
δ = Unit Weight of Sliding Mass, kg/m^3 (lb/ft^3)
d = Vertical Thickness of Sliding Mass, m (ft)
α = Slope Angle, (degrees; 3 to 1 side-slopes is 18°)
r_u = Pore Pressure Ratio (none)
c_s = Horizontal Acceleration, Seismic Event (0.12 g)
ϕ = Effective Friction Angle of Sliding Mass (36°).

The parameters (c,ϕ,d,δ) are based on laboratory test data of the existing soils at the proposed project site and on the proposed geosynthetics to be used when the facility is built. To be conservative, the effective cohesion is assumed to be zero, and when determining the static factor of safety, the horizontal acceleration is also zero. For the dynamic analysis, a 0.12 g horizontal acceleration is used at the Hanford Site as required by the Hanford Plant Standards (18). The factor of safety for this facility was calculated for the subgrade and the interface between each and every liner to determine the critical interface. The critical interface is the interface that is most likely to fail, or the one with the lowest factor of safety. The critical interface for this specific project proved to be between the operations layer and the uppermost geotextile,

with a static and dynamic factor of safety of 1.8 and 1.3, respectively, which is within the minimum acceptance criteria.

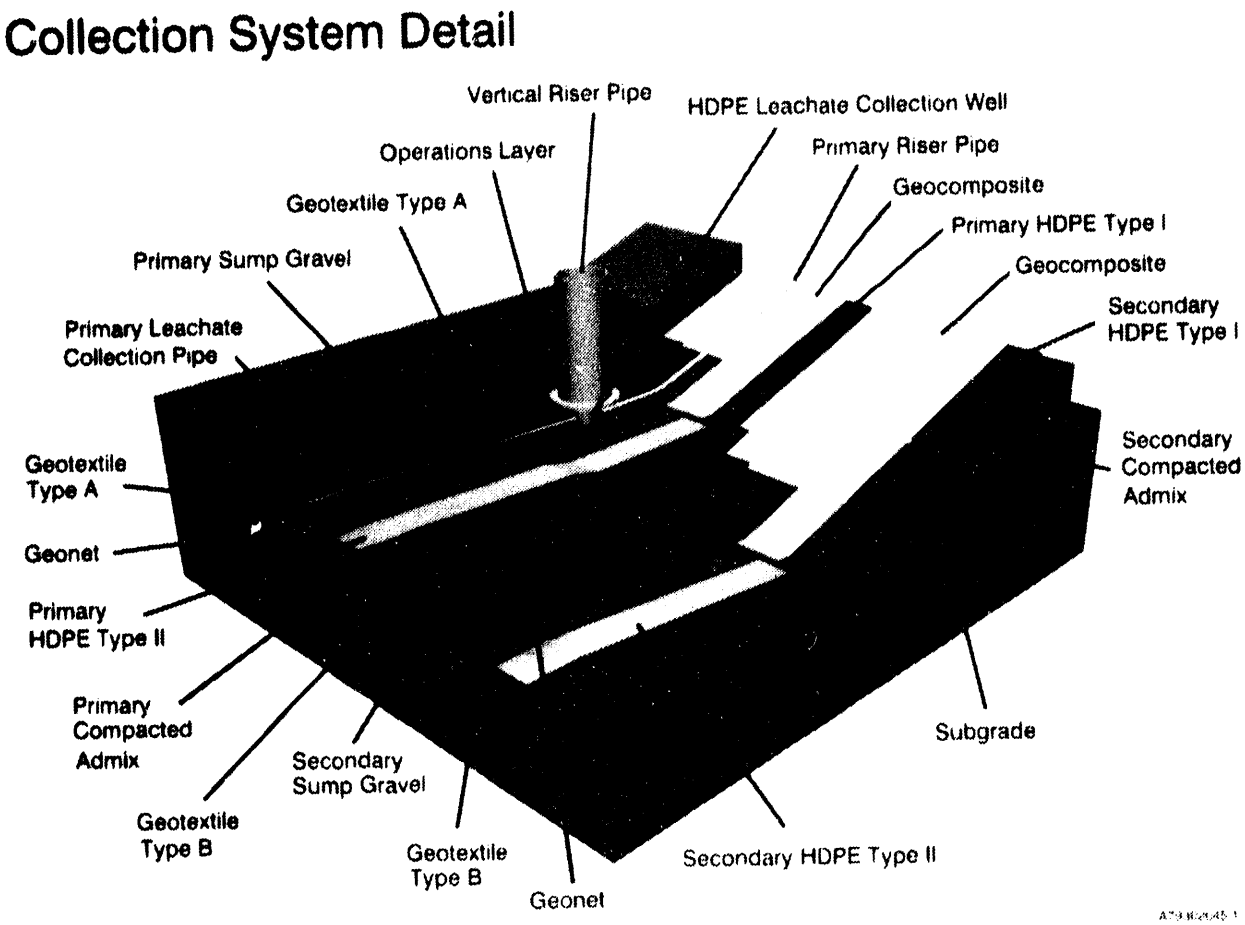


Figure 3. Radioactive Mixed Waste Land Disposal Facility multilinear cross section.

Research and experience have shown that desiccation cracks can occur in soil-bentonite liners under geomembranes. Desiccation cracking (of the admix) may occur under the geomembrane liners when either (1) the liner is not in tight contact with the admix and moisture leaves the admix to collect in the adjacent air space or (2) the liner is subjected to wide temperature fluctuations (i.e., freeze-thaw cycles). The operations layer will act as a weight to keep the geomembrane in tight contact with the admix and provides a protective layer for the underlying liners during waste placement. It also minimizes the potential for desiccation cracking of the primary and secondary admix liner by acting as a thermal insulator.

9090 Liner Leachate Compatibility Test

The proposed geosynthetic and admix liners for the RMW landfill were tested for chemical resistance to synthetic leachate in accordance with EPA method 9090 (19). The goal of this testing is to ensure that the proposed liners will not be adversely affected by any potential leachate, if the liners were exposed to a worst case leachate concentration. The synthetic leachate (pH = 9.2) is developed based on the packaging approaches, including stabilization agents of anticipated waste streams emplaced in the landfill. Under this

method, samples of geosynthetic materials and laboratory samples of compacted admix were immersed in a synthetic leachate at temperatures of 23 and 50 °C. A portion of the geosynthetic samples is removed at intervals of 30, 60, 90, and 120 days and is tested to determine any changes in physical and mechanical properties. For this specific project, the standard EPA 9090 test procedure (19) was modified; some samples were irradiated while immersed in the leachate to simulate the effects of the radioactive component of RMWs. The irradiated samples were exposed to gamma radiation for about two hours and received a total dose of 50,000 rad, which is considerably higher than the actual expected dose. The important question is, "Does the thermal loading caused by the radioactive constituents of the waste, or the radiation itself, or the combination of the radiation and the hazardous constituents (pH=9.2) cause the liners to deteriorate?" In both the irradiated and nonirradiated cases, the HDPE showed no statistically significant change in the properties of the liner materials. The temperature changes caused by the radioactive component are anticipated to be less than 1 °C. Additionally, laboratory permeability (flexible wall permeameter) testing, using the same synthetic leachate, was conducted on samples of compacted admix, as an added level of assurance (not required). Based on the results of this testing, the admix showed a significantly higher permeability to synthetic leachate than to site water. However, admix containing 12% sodium bentonite clay showed a permeability to leachate that was 3 to 10 times (varied between samples) lower than the regulatory acceptance criteria of 1×10^{-7} cm/s.

Leachate Collection and Handling

The leachate collection and removal system is designed to be capable of collecting and removing leachate to control the hydraulic head on the liner. Leachate is routed to the east end of the trench where the leachate collection well is located. Several pumps are used to remove leachate to a storage tank located abovegrade. The leachate collection and removal system consists of two low-capacity submersible pumps, a high-capacity pump (worst case rain storm), a transfer pump, a 37,850-L (10,000-gal) collection tank, 6.1 m (20 linear ft) of 76.2-cm (30-in.) HDPE (collection well-vertical riser), approximately 67 m (220 linear ft) of 20.3-cm (8-in.) HDPE pipe (removal piping), 378 m (1,240 linear ft) of 10.2-cm (4-in.) perforated (collection piping) HDPE pipe, approximately 488 m (1,600 linear ft) of 10.2-cm (4-in.) HDPE (collection piping) pipe, and 128 m (420 linear ft) of 5.08-cm (2-in.) HDPE pipe. Located inside the 5.08-cm (2-in.) HDPE pipe are level sensors, with a level transducer and a current sensitive relay. The relay is controlled by current from the level transducer and turns the submersible pumps on and off. For a worst case rain scenario, a high-capacity pump will be activated. This self-priming pump has independent high and low on/off levels controlled by mercury float switches in the vertical riser pipe.

WASTE FACILITY FILL PLAN

Engineering studies will be completed to determine the "optimal" waste fill plan. Optimal refers to the largest possible waste volume of the landfill without impacting the performance of the landfill. Waste packages will be placed in the landfill by forklift or crane and across the entire bottom layer of the landfil' Once an entire layer or lift of waste packages has been emplaced, a layer of soil or cement-like backfill will be used between and above the containers to provide an operating surface for the next layer of waste. It is expected that three to four tiers of waste will be accommodated. Each lift is emplaced completely before initiating a subsequent lift so that the driving forces of emplaced waste on the slope do not exceed the resisting forces of the waste on the floor and possibly initiate a slope failure. The void areas between each layer of waste and between waste containers will be filled with soil or cementations backfill. The purpose of the backfill is to provide a stable waste matrix in the trench and to protect the waste packages while providing a working surface for equipment and subsequent lifts. Some commercial names for the cementations backfill are Controlled Density Fill (CDF) or K-Krete. CDF is essentially a low-strength concrete composed of fly ash, portland cement, aggregate, and water. It was developed by engineers at Detroit Edison who sought to find a use for fly ash, a byproduct of their coal burning power plants. K-Krete was developed by Detroit Edison and Kuhlman Ready/Mix. At the Hanford Site, CDF is being

evaluated, and fly ash from the two coal-fired steam plants is being considered. Assuming the fly ash can be used as part of the cementations mixture, it would eliminate or reduce the problem of disposing of fly ash at the Hanford Site, and represents a "good" waste minimization program.

DISPOSAL FACILITY SCHEDULE

The RMW disposal trench is scheduled to be constructed during 1994. Trench excavation will occur early in the year February 1994. Installation of the geomembranes and liners will occur during the dryer warmer months because of the temperature and moisture sensitive nature of the liner installation process. The operating life of the landfill is 20 years maximum, with a 50-year design life. A 30-year post closure period is planned after the trench is filled. Actual operational trench life will depend on the rate of waste emplacement.

CLOSURE DESIGN AND POST CLOSURE MONITORING

The location of the RMW disposal trench is within the 218-W-5 Burial Ground. This trench is in the vicinity of past waste disposal activities and future or planned waste management activities. Closure of this trench will be accomplished as part of closing a larger area of adjacent contiguous burial grounds.

The cover design will comply with the requirements for dangerous waste disposal as defined in 40 CFR 264 (8) and WAC 173-303 (10). The cover will be designed to control water infiltration. The cover design will include a vegetative surface soil layer, a high permeable gravel layer to remove water, and a flexible membrane infiltration liner with a soil-bentonite liner underneath it. The slope of the cover has not been designed yet. It may be a 33% slope (3H:1V), 25% (4H:1V) or 10% (10H:1V) with rip-rap to minimize erosion. The slope of the cover will affect the volume capacity. Obviously a 33% slope will maximize landfill waste capacity. However, at 2 or 3 percent slopes, wind and water erosion becomes a factor that must be considered, and the uppermost surface must contain coarser material that will still support vegetation. A drainage system around the cover will be used to move any precipitation away from the cover.

At closure, a radiological site survey will be performed to characterize the site grounds. This survey will be part of the permanent decommissioning record. Leachate and groundwater monitoring will give an indication of the integrity of the liners and closure cover. Leachate is not expected to accumulate in the trench other than precipitation during operations. No leachate is anticipated after trench closure. Monitoring of the trench will be performed for 30 years after trench closure.

MIXED WASTE DISPOSAL FACILITY PERMITTING PROCESS

The RCRA requires cradle-to-grave management of wastes; owners and/or operators of TSD facilities are required to obtain permits for continued operation of facilities. The purpose of RCRA is to reduce or eliminate the generation of hazardous waste and to treat, store, and dispose of hazardous waste so as to minimize the present and future threat to human health and the environment (waste minimization is a goal of RCRA).

The Low-Level Burial Grounds Dangerous Waste Permit Application (20) is an example of a RCRA Part A and B permit application, submitted to Washington State for dangerous waste operations at the low-level burial grounds. The Part B permit provides documentation for disposal of RMW at the Hanford Site. Currently, the Hanford Site is covered by RCRA interim status regulations. Construction and operation of the RMW disposal trench will be initiated under interim status and the above permit application. Once the

regulators approve the Low-Level Burial Grounds Dangerous Waste Permit Application, the Hanford Site will have final operating status for waste disposal.

An important component of a permit for a disposal facility of this nature is the CQA Plan. A project-specific CQA Plan (21) must be developed for the construction of the facility if an operating permit is to be granted. Guidance for Quality Assurance during construction is outlined in EPA's Technical Guidance Document (12). The CQA Plan is analogous to an inspection plan used during construction and identifies appropriate documentation to ensure regulators that the facility has been constructed in accordance to the applicable design criteria, plan, and specifications. This plan will require the construction contractor to repair any deficiencies encountered before construction completion. In some cases in the United States, failure of a facility of this nature to perform as intended has been linked directly to inadequate construction quality assurance activities. For this reason, an appropriate CQA Plan, similar to reference 21, must be developed for a project of this kind.

The final status permit requires that landfill owners and operators strictly follow the permit. In addition to what is submitted in the permit application and the requirements under interim status, the state may add special conditions to the permit. These conditions can severely limit the operation or add administrative controls.

CONCLUSION

The solid waste program provides a 30-year forecast of solid waste volumes by waste type. Environmental restoration and cleanup of the Hanford Site is expected to take more than 30 years. Environmental restoration and new programs at the Hanford Site will generate solid radioactive waste for disposal during this time frame. The landfill described above and ones similar will be built as appropriate to support these forecasted solid RMW volumes.

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THE RELATIONSHIP BETWEEN THE RESOURCE CONSERVATION AND RECOVERY ACT AND THE STORAGE AND DISPOSAL OF SPENT NUCLEAR FUEL AND HIGH-LEVEL WASTE

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ABSTRACT. This paper addresses the potential applicability of the requirements of the Resource Conservation and Recovery Act (RCRA) to the disposal of spent commercial nuclear fuel and of high-level (vitrified) radioactive waste. The Atomic Energy Act of 1954, as amended, and the associated regulations issued by the U.S.Nuclear Regulatory Commission provides many requirements that apply to these waste forms and largely, if not entirely, pre-empts the applicability of RCRA. The RCRA would apply only to the non-radioactive components of these wastes, and then only in respect to hazardous components. In view of these restrictions it becomes important to evaluate whether any components of spent fuel or high-level waste are toxic, as defined by the RCRA regulations. Present indications are that they are not and, hence, the U. S. Department of Energy is proceeding on the basis that these wastes and others that may be generated in the future are non-hazardous in respect to RCRA definitions.

INTRODUCTION

From time to time questions have arisen in respect to the applicability, or lack thereof, of the Resource Conservation and Recovery Act, Subtitle C (RCRA) (1) to the disposal and storage of civilian spent nuclear fuel (SF) and defense high-level radioactive waste (HLW). Some parties have argued that only the provisions of the Atomic Energy Act of 1954 as amended (AEA) (2) apply to these materials, whereas others, for example the State of Nevada, believe that the hazardous waste provisions of RCRA (Subtitle C) should apply. This paper provides some details of these Acts in relation to the nature of civilian spent fuel and HLW and the potential applicability of RCRA to these wastes.

HAZARDOUS WASTE REQUIREMENTS OF THE RESOURCE CONSERVATION AND RECOVERY ACT

Title 40 of the Code of Federal Regulations, Part 261, Identification and Listing of Hazardous Waste (3), defines various categories of solid hazardous waste and exclusions of various materials from some parts of the regulations. Of particular note are the exclusions at 40 CFR 261.4(a)(ii)(4) of "Source, special nuclear or byproduct material as defined by the Atomic Energy Act of 1954, as amended." Examination of the definitions of these materials in the AEA makes it quite clear that at least the radioactive portions of HLW, low-level (LLW) and other forms of radioactive solid waste, are excluded from RCRA regulations. It is less obvious, however, whether other components of these wastes fall under RCRA. A guidance document

(4), issued jointly on January 8, 1987, by the U.S.Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC) defined mixed LLW waste as "...waste that satisfies the definition of low-level waste in the LLW Policy Act Amendments Act of 1985 and contains hazardous waste that either (1) is listed as a hazardous waste in subpart D of 40 CFR Part 261 or (2) causes the low-level waste to exhibit any of the hazardous waste characteristics identified in subpart C of 40 CFR Part 261." This document states that "...NRC and EPA consider that only the radionuclides themselves are exempt from RCRA."

One might reasonably assume that the EPA and NRC will eventually sanction a stance with respect to HLW or SF that resembles that for LLW. In that case the requirements at 40 CFR 261.4(b), Solid wastes which are not hazardous wastes, will become relevant. This section identifies various solid wastes that are not hazardous waste, and refers to criteria and tests to determine the proper classification. A few of the many exclusions under this section are household wastes, mine wastes returned to the mine site, and wastes that are not toxic as determined through application of the Toxicity Characteristic test. Rather clearly, only the last of these may apply to SF or HLW. It will, therefore, be prudent to show, if possible, that these waste forms are not toxic.

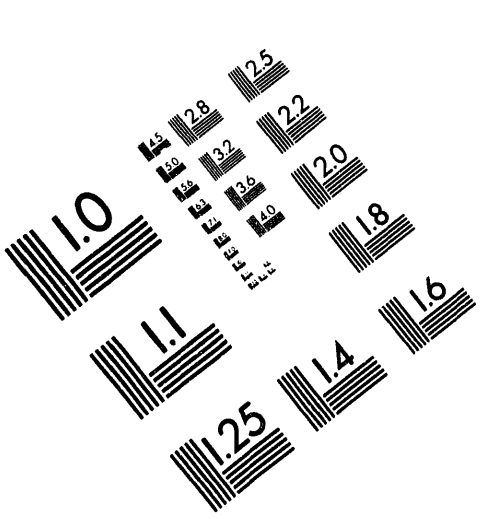
Subpart C of 40 CFR 261 defines the characteristics of hazardous waste as promulgated by this regulation. These characteristics are categorized as ignitability, corrosivity, reactivity and toxicity. As defined in this Subpart, corrosive wastes include only liquids and reactive wastes must be gaseous or capable of producing gases, e.g. by explosion. Title 10, Code of Federal Regulations, Part 60.135(b) specifically prohibits explosive, pyrophoric, chemically reactive materials and free liquids materials from containment within a HLW package. Thus, only the toxicity question remains. The waste is considered toxic if the extract obtained by prescribed methods (e.g. as defined in Appendix II of 40 CFR 261) contains any of the contaminants listed in Table 1 of 40 CFR 261.24 equal to or greater than the value listed. Most of the substances in this table are organic compounds, which will not be present in SF or HLW. The inorganic materials include only the elements arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), selenium (Se) and silver (Ag).

RELEVANT CHARACTERISTICS OF SPENT CIVILIAN NUCLEAR FUEL AND HIGH-LEVEL WASTE

As noted above, the NRC requires that these waste forms be solid, non-explosive or pyrophoric, and chemically non-reactive. This eliminates from consideration most aspects of the RCRA regulations. Only toxicity remains as a potential reason to apply RCRA requirements. In this regard it will be important to determine the leachability of these waste forms in respect to specified elements. None of the listed toxic organic materials will be present in view of the chemical characteristics, manufacture and utilization of SF and HLW.

With the exception of chromium the elements As, Ba, Cd, Cr, Pb, Hg, Se, and Ag are initially absent from SF (6). Chromium does occur as a component of the zircaloy cladding of the fuel. Small amounts of all or most of these elements are, however, produced during nuclear transformations in the reactor. The trace amounts (e.g., ppb) fall well below the EPA's "toxic" threshold. RCRA listed contaminants have not yet been identified as components of high-level, or vitric, waste. One of the principal reasons for selecting these waste forms for disposal in a repository is their resistance to leaching, dissolution or degradation. The U. S. Department of Energy (DOE) has conducted numerous tests that indicate the inertness of these waste forms over time frames greatly in excess of the times specified directly or indirectly in 40 CFR 261. The Department is accordingly proceeding on the basis that neither SF nor HLW is hazardous.

The DOE has evaluated its programs and plans in accordance with Section 803 of the Energy Policy Act of 1992 (7). This involved assessing the adequacy for managing additional wastes that may be generated in the future, including new commercial nuclear power plants and other sources. Because these additional sources will not in general exist for many years into the future and because current programs and plans



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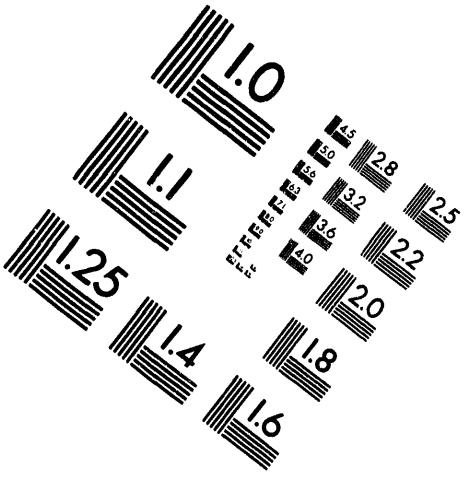

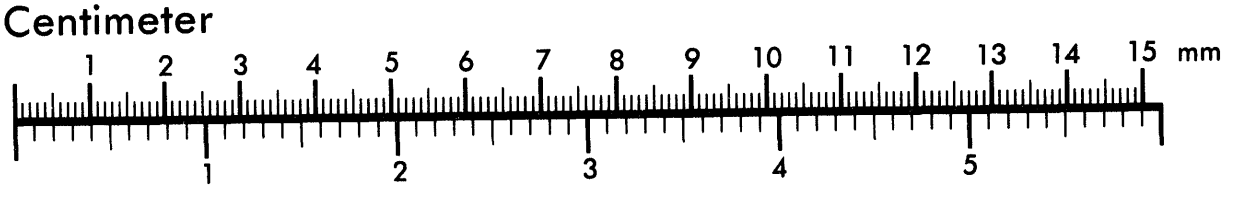

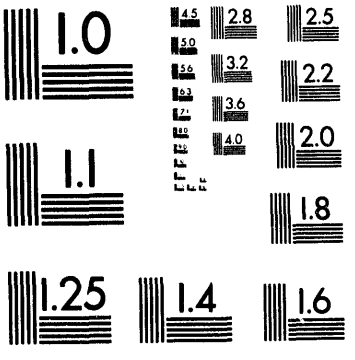

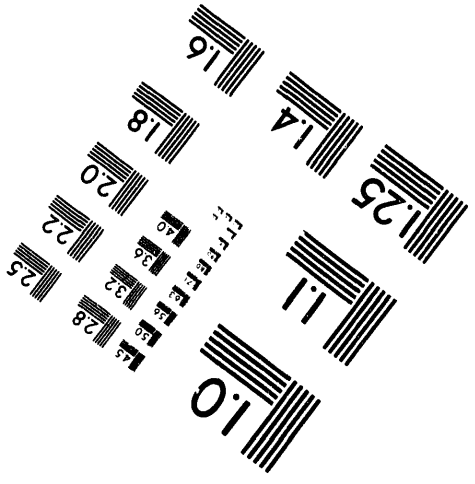

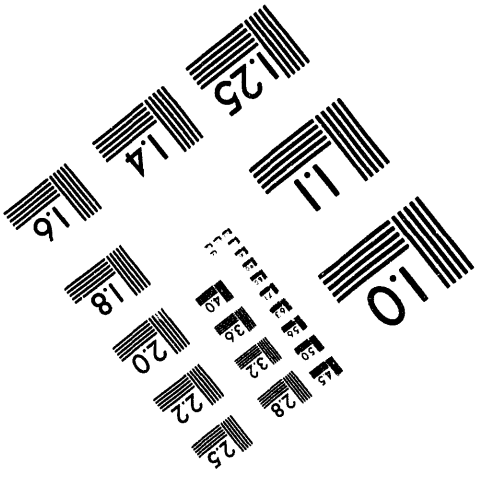

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incorporate significant flexibility, the DOE has concluded that provisions for the management of these potential additional volumes or categories of HLW will suffice. In other words there will be sufficient time to make changes in needed respects in the future.

SUMMARY

A significant question in respect to the disposal of spent nuclear fuel and high-level radioactive waste is what constitutes sufficient regulation. The NRC, in 10 CFR 60 (5), provides stringent requirements, both in respect to what may be placed into a waste package, the character of the waste placed therein, the characteristics of the geologic environment, and the EPA, in 40 CFR 191 (8), provides the length of time over which a repository must prevent contamination of the accessible environment. These requirements eliminate the need to apply any of the requirements of the RCRA. Present indications are that these wastes are non-hazardous according to 40 CFR 261 specifications in respect to toxicity. In this case the additional regulation, complexity of compliance, and costs of implementing RCRA in addition to the Atomic Energy Act of 1954, as amended, would appear to be redundant and unnecessary. The DOE is accordingly proceeding on the basis that these wastes are non-hazardous in respect to the definitions incorporated into 40 CFR 261.

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CHAPTER 10

Organic Treatment Technologies

TREATING CONTAMINATED ORGANIC COMPOUNDS USING THE DETOX PROCESS

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ABSTRACT. Waste matrices containing organic compounds, radionuclides, and metals pose difficult problems in waste treatment and disposal when the organic compounds and/or metals are considered to be hazardous. This paper describes the results of bench-scale studies of DETOX applied to the components of liquid mixed wastes, with the goal of establishing parameters for designing a prototype waste treatment unit. Apparent reaction rate orders for organic compounds and the dependence of apparent reaction rate on solution composition and the contact area were measured for vacuum pump oil, scintillation fluids, and trichloroethylene. Reaction rate was superior in chloride–based solutions and was proportional to the contact area above about 20 g/kg loading of organic material. Oxidations in a 4-L volume, mixed bench-top reactor have given destruction efficiencies of 0.999999+ g/g for common organic compounds. Reaction rates achieved in the mixed bench-top reactor were one to two orders of magnitude greater than had been achieved in unmixed reactions; a thoroughly mixed reactor should be capable of oxidizing 10 to 100+ g of organic material per L–hr. Results are also presented on the solvation efficiency of DETOX for mercury, cerium, and neodymium, and for removal/destruction of organic compounds sorbed on vermiculite. The next stage of development will be converting the bench-top unit to continuous processing.

INTRODUCTION

An efficient wet oxidation process can be an effective tool in the controlled treatment/volume reduction of many waste types, including mixed wastes. The DETOX process, which uses iron(III) oxidant in an aqueous acid solution (1,2), has been shown in previous studies to apply to a variety of waste types, oxidizing waste organic compounds to carbon dioxide while containing and concentrating metals in the acidic catalyst solution. Cerium and neodymium have been used in our studies as surrogates for plutonium and uranium, because they should have similar chemistries in the DETOX catalyst solution. Because many contaminated organic wastes contain very little radioactive material, the volume reductions that can be achieved are great, and, in many instances, a large volume of organic waste can be converted to a small volume of radioactive–only solid inorganic waste. The low temperature process produces no NO_x, SO_x, dioxins, or furans, and has relatively low power usage. To further define the parameters of a practical waste treatment unit using DETOX, additional development studies have been conducted during the past year. The ability of the process solution to treat vermiculite, and to solvate mercury, neodymium, and cerium was investigated. (More detailed metals studies are now in progress, as well as studies on the ability of the process to treat contaminated soils.) The effects of organic compound loading and contact area between the organic compound and the oxidizing solution have been determined for vacuum pump oil, scintillation fluids, and trichloroethylene to establish desirable loading values and mixing rates for a prototype waste

treatment unit. A 4-L volume, stirred bench-top reactor was operated in batch mode to determine reaction rates and destruction efficiencies at larger process volume under mixed conditions. The bench-top reactor also provided an opportunity to determine the suitability of some materials and components for a prototype waste treatment unit and to measure the operating pressures and vapor composition of the DETOX solution. In the development studies described in this paper, no major problems in operating the process were encountered, indicating that it will be desirable to proceed to continuous processing studies in the bench-top unit as a test bed for engineering and design of the prototype waste treatment unit.

EXPERIMENTAL

The reaction vessels used in these studies were of three types. Small test volumes were used in Parr Instrument Company (PIC) Model 4749 23-mL general purpose bomb. Intermediate size studies were conducted in PIC Model 4751 125-mL general purpose bombs. The bench-scale studies were conducted in a PIC Model 4551 one-gallon (~4-L) pressure reaction apparatus with entrained gas stirrer.

The catalyst solution and other reagents were prepared from "reagent" or "ACS" grade materials and 10 MΩ—cm deionized water. Iron chloride solutions used in the bench-top tests were prepared from electrolytic-grade iron, reagent-grade hydrochloric acid, and electronic-grade hydrogen peroxide to oxidize iron(II) to iron(III) before use. Samples of Hydrocount™ and Ready Value™ scintillation fluids, and Duoseal™ vacuum pump oil were provided by Los Alamos National Laboratory (LANL) and were used as-is. Trichloroethylene was all reagent-grade material from stock at Delphi Research, Inc. (Delphi). Organic compounds spiked with metals were prepared using mercury metal, mercuric oxide, neodymium isopropoxide, and cerium naphthanate solution. A representative sample of the mixture was used for the metal solvation studies, or, for mercury metal, the entire mixture was used. Gases used in gas chromatography analysis were all "zero" grade. The oxygen used for pressuring the reaction vessels was standard grade.

Blank vermiculite was prepared by baking a commercial vermiculite at 523 K for 24 hours and was subsequently stored in a clean glass bottle; gas chromatographic purge/trap analysis of off—gas from the heated (453 K) blank vermiculite demonstrated the absence of detectable volatile organic compounds. Spiked vermiculite was prepared by suspending a small container of the blank vermiculite in a sealed bottle containing Hydrocount™, Ready Value™, or trichloroethylene for at least 24 hours to achieve an equilibrium concentration of sorbed organic; gas chromatographic analysis was used to establish the preoxidation levels of sorbed organic compounds.

For each oxidation the bombs were loaded with 10 mL, 50 mL, or 1500 mL of the primary catalyst solution, followed by addition of a weighed amount of cocatalyst and a measured amount of the organic. The 125-mL bombs and the bench-top reactor were pressurized with 690 kPag (100 psig) of oxygen before heating. The 23-mL and 125-mL bombs were placed into an oven preheated to the desired temperature; at the end of the allotted reaction time, the bombs were removed from the oven and allowed to cool in a shallow (about 1.0 cm) water bath. The bench-top reactor was heated by a heater well into which the reactor body was placed; the bench-top reactor was not actively cooled and generally required several hours to cool to near room temperature from its operating temperature of 473 K.

Iron(II) was titrated with cerium(IV), using 1,10—phenanthroline as an indicator. Gas chromatographic analysis for gases was performed using a gas sample injection loop into a Carbosphere™ column with detection by thermal conductivity. Gas chromatographic analysis for volatiles was performed by purge—trap technique, using a standard EPA Method 8240 (3) packed column and an FID detector; the residual volatile material was identified by retention time. Volatiles and semivolatiles were analyzed for the destruction efficiency studies by Environmental Protection Agency Methods 8240 and 8270 (3) at an independent commercial analytical laboratory. Analyses for mercury were conducted by cold vapor atomic absorption,

with sample spiking to correct for matrix effects. Neodymium and cerium were analyzed by inductively coupled plasma spectrophotometry at an independent commercial analytical laboratory.

RESULTS

DETOX Solution Composition

A sulfate—based medium and a chloride—based medium are the two primary media that can be used for the DETOX process in application to hazardous organic compounds. For radionuclides such as uranium and plutonium, it was felt that a chloride—based medium would have superior characteristics. A series of studies was undertaken to identify an optimum composition for a chloride—based DETOX solution, and it was found that, although initially the chloride ion decreases the reaction rate constants for oxidation of organic compounds, at higher concentrations the oxidation rate constant began to increase again (Fig. 1). Using chloride at high concentrations also allows a large amount of iron(III) to be kept in solution, further increasing the total amount of oxidation that is achieved. The result is an increase of at least a factor of ten in total amount of oxidation obtained in a concentrated chloride DETOX solution versus a sulfate—based solution.

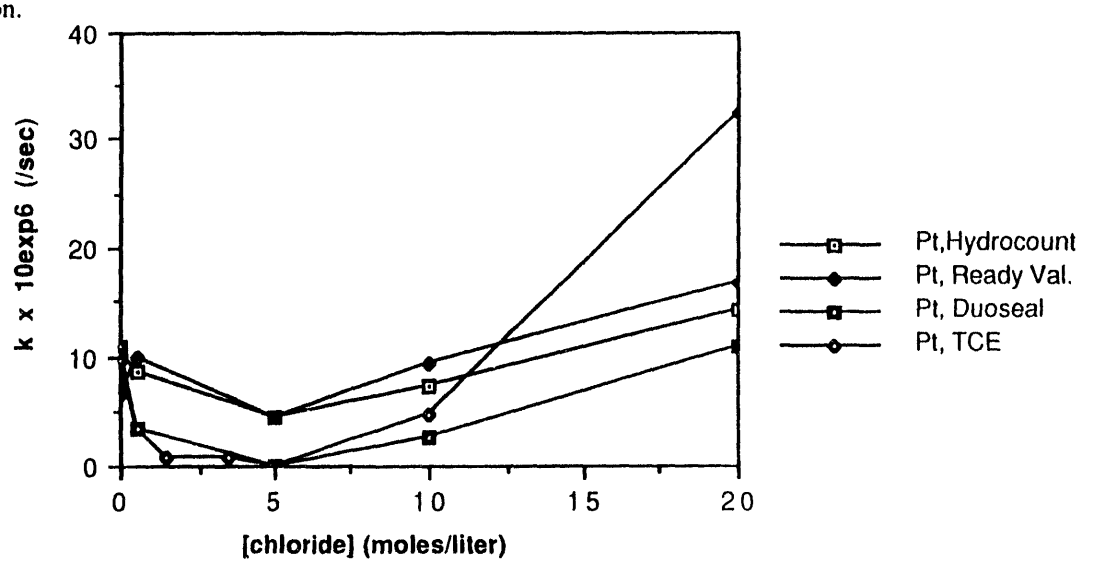

Figure 1. Reaction rate constants Vs [Cl] for oxidation of selected organics by Iron(III).

Solubility of Mercury, Cerium, and Neodymium

Three metals of interest in mixed waste at Los Alamos National Laboratory are mercury, plutonium, and uranium. Cerium and neodymium have been used in our studies as substitutes for plutonium and uranium, because they should have similar chemistries in the DETOX catalyst solution. Solubilities for the surrogate metals neodymium and cerium appear to be in keeping with the solubilities to be expected from the chlorides of these metals, with neodymium soluble to the extent of about 80 g/L catalyst solution, and cerium soluble to the extent of about 200 g/L catalyst solution. Changes in acidity had little effect on the solubilities of either of the metals over the range of 0.5M to 2.0M H+. Neodymium solubility was adversely affected by sulfate anion; it has been found advantageous to scavenge sulfate from the DETOX solution with calcium. When organic compounds containing cerium and neodymium were oxidized in the catalyst solution, no amounts of cerium or neodymium were found in the solid residues (in fact, there was no significant solid residue after oxidations). The detection limits for the analytical method used for these two metals give a minimum of 0.97 g/g solvation, but the actual values are probably considerably higher.

Mercury is soluble in the DETOX chloride–based solution to the extent of about 400 g/L. Mercury solubility was not affected by minor changes in acidity or by sulfate anion concentrations of 0.2M. Phosphate anion at 0.2M reduced mercury solubility to about 300 g/L. Mercury was tested as a contaminant in vacuum pump oil at loadings of approximately 100 μg mercury as mercuric oxide in 10 mg of oil, and at 12-15 mg mercury as mercury metal in 10 mg oil. The amount of mercury found in solids from the oxidation ranged from less than 0.15 μg for the tests with 100 μg/10 mg loading to around 1 μg for the tests with 12-15 mg/10 mg loading, or at least 0.9998 g/g solvation of the mercury. It is suspected that the small amount of residual mercury seen in the solids was due to incomplete rinsing.

Treatment of Contaminated Vermiculite

Sorbent and mineral materials contaminated with hazardous organic compounds and radionuclides can be problem wastes. It was of interest to determine the ability of the DETOX solution to remove or destroy scintillation fluid solvents and trichloroethylene from vermiculite. Loadings on the vermiculite ranged from 33 mg/kg for trichloroethylene to 200 mg/kg for pseudocumene (1,2,4-trimethylbenzene). After 24-hour oxidations in unmixed 23-mL bombs, the amount of sorbed organic remaining on the vermiculite ranged from 150 μg/kg for trichloroethylene to 30 μ/kg for pseudocumene and o-xylene. It is believed that the actual amount remaining was less than that analyzed, because the Teflon™ liners in the 23-mL bombs absorb volatile organic materials during heating and then release them back into the bomb upon cooling.

Effects of Organic Loading and Contact Area

The reaction rate of the oxidation reaction depends not only on iron(III) concentration but also on the concentration of organic material and, at least in some instances, the area of contact between the organic material and the DETOX catalyst solution. Figure 2 shows results from studies of organic material loading versus oxidation rate in unmixed reaction bombs. The data is fitted by a logarithmic curve that gives the pseudo-order of the reaction in the organic compound (the exponential factor) and a multiplicative constant

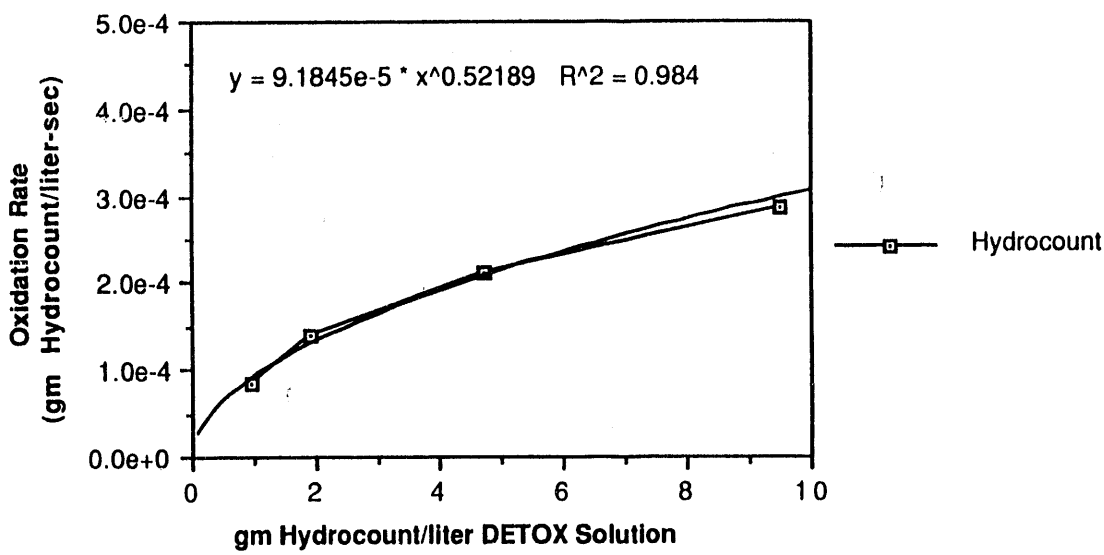

Figure 2. Hydrocount ™oxidation rate Vs loading in DETOX solution at 473 k.

that is equal to the product of the apparent reaction rate and the iron(III) concentration. Pseudo–orders were 0.52 for Hydrocount™, 0.31 for Duoseal™, and 0.25 for trichloroethylene. Several factors complicate the relationships found in these studies. The surface area of contact between the catalyst solution and the organic compound (that is, mixing), the solubility of the organic compound in the catalyst solution, the vapor pressure of the compound, and the head space volume of the reaction vessel should all affect the

relationship between loading and apparent oxidation rate. Reaction rates at greater loadings will be controlled by the bulk diffusion rate of iron(III) to the reaction surface; in a well-mixed system, the apparent reaction rate would be greater because of the thinner diffusion layer at the contact surface. Increased reaction rates at higher loadings would increase the apparent reaction orders; coal gasification studies with iron(III) oxidation solutions in well-mixed reactors have given a pseudo—order of near 1.0 for organic compounds (4). In a thoroughly mixed reactor, the solubility of the organic material should have little effect on the apparent reaction rate unless the organic material is quite soluble in the catalyst solution (4,5). The loading, the vapor pressure of the compounds, and the headspace of the bomb will combine to create a discontinuity in the apparent reaction rate at that point at which there is sufficient material to allow liquid to exist in contact with the DETOX solution. The liquid compound is of much greater concentration at its area of contact than is the vapor.

These results allow estimates of the time required to achieve a given amount of oxidation and of the time required to reduce the concentration of an organic compound to a given level. Calculations indicate that to reduce a catalyst solution from 1.0 g/kg concentration to 1 x 10—6 g/kg, concentration will require about 20 hours for Duoseal™, 6.3 hours for Hydrocount™, and 1 hour for TCE. This type of calculation would be valuable to estimate the time required to reduce the concentration of the organic compound to desirable levels at the conclusion of a waste-processing run, although one would not normally be operating a waste treatment unit in such a feed—starved condition.

The relationship between contact surface area and apparent reaction rate was explored in two series of studies. One used 23-mL bombs, with the volume of catalyst solution varying from 10 mL to 1 mL while the amount of organic compound and the surface area of contact between the organic compound and the catalyst solution were kept constant. In these tests, the total amount of oxidation, as measured by generation of iron(II), was not changed over a tenfold variation in solution volume; this result tends to eliminate solution volume as a factor in determining the reaction rate.

To further clarify the relationship between the concentration of the organic compound, surface area of contact, and the apparent reaction rate, a second series of tests was conducted using HydrocountTM in 125-ml bombs. By tilting the bombs at a 45° angle, an increase in contact area from 11.4 cm^2 to 16.1 cm^2 could be obtained. The bombs were loaded with 25-ml of catalyst solution and amounts of Hydrocount™ from 47.5 mg to 0.95 g (Fig. 3). At lower loadings, the reaction rate appears to depend solely on the

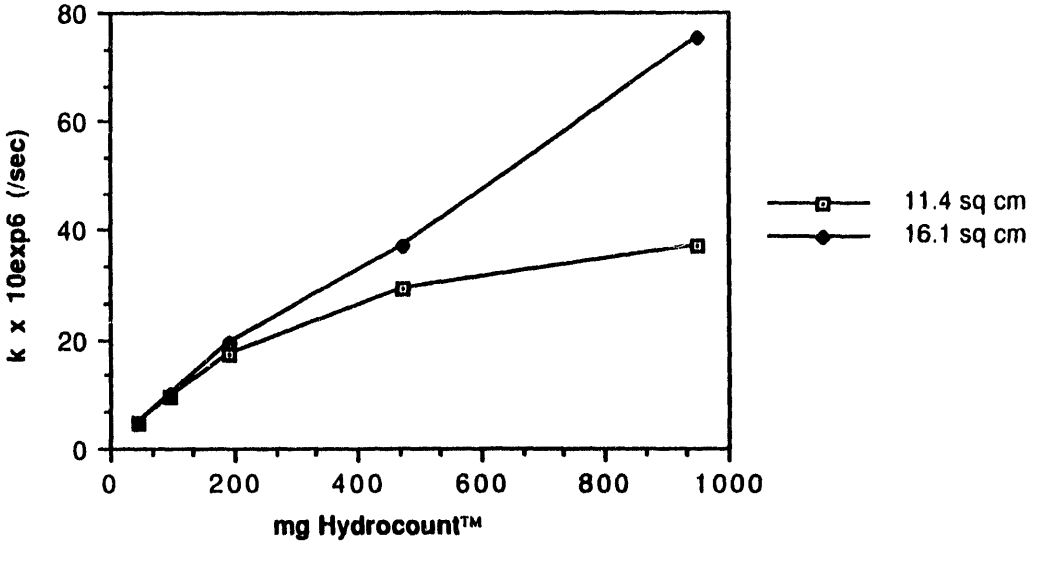

Figure 3. Apparent reaction rate constants Vs organic loading at 473 k.

amount of organic compound. At greater loadings, the reaction becomes dependent on contact surface area. These results are consistent with a reaction that is controlled by diffusion (which in turn depends on concentration) at lower loadings and by iron diffusion (which depends on contact surface area) at greater loadings.

Because the catalyst solution in these studies is unmixed, the availability of iron(III) at the surface is controlled by the rate of diffusion of iron(III) in the catalyst solution, which is consistent with Lature values for iron(III) diffusion in aqueous solutions. From the data here, the reaction rate becomes dependent on iron(III) diffusion at about 100—200 kPa vapor pressure for the organic compound. Thus, a great increase in reaction rate should be expected in a mixed reactor because of both thinner diffusion layers and, if the organic compound is a liquid or vapor, increased contact area. Figure 4 demonstrates this increase in reaction rate if the ratios of surface area to volume obtained in the 23-mL bomb tests are converted to contact area for a given particle size of organic material at a 50 g/kg loading for Ready Value™ scintillation fluid.

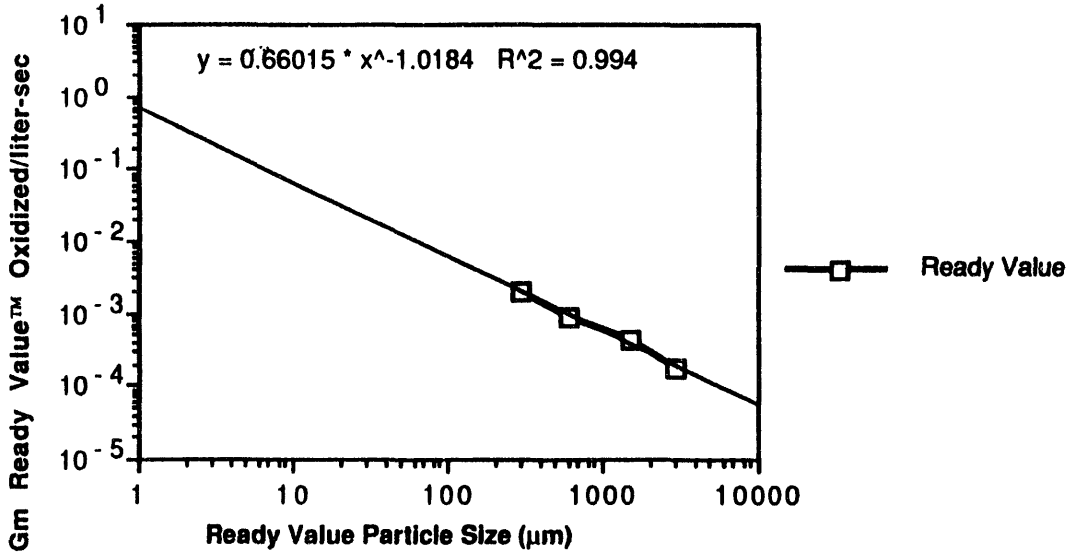

Figure 4. Oxidation rate Vs particle size for ready value at 5% v/v loading and 473 k.

Oxidation Efficiencies

Oxidation efficiency studies for Hydrocount™, Ready Value™, Duoseal™, and TCE were done in both unmixed 125-ml bombs and in the stirred 4-L reactor.

Oxidations in unmixed 125-ml bombs were done for 24 hours to obtain a fairly complete oxidation of the organic compounds. From 95 mg to 438 mg of the organic compounds were oxidized in these studies. Oxygen consumption and carbon dioxide production indicated essentially complete oxidation to carbon dioxide. Negligible amounts of iron(II) were measured in the post—oxidation solutions; thus, the iron was kept in the (III) state by the oxygen in the bombs. Samples of the post—test solutions were submitted to an independent analytical laboratory for analysis of volatile and semivolatile organic compounds. Results showed that greater than 0.999997 g/g of the o—xylene and 1,2,4—trimethylbenzene had been destroyed and that 0.99995 g/g of the TCE had been destroyed. Some amounts of other organic intermediates were seen, giving absolute destruction efficiencies of about 0.99 g/g in these tests.

Oxidations of organic compounds in the 4-L stirred bench-top reactor were conducted over much shorter periods than those in the unmixed bombs and with significantly greater amounts of organic compounds. Preliminary oxidations with n—butyl acetate as the organic oxidized from 7.875 g to 13.125 g of organic for one and three hours, respectively. Destruction efficiency for the parent compound was >0.999999 g/g. Some intermediates were seen in the catalyst solution, giving an absolute destruction of all organic material of about 0.999 g/g. The apparent reaction rate constant for oxidation of n—butyl acetate was about 1 x 10—4/sec at 423 K at a relatively low loading of 2 g/kg. Loading was limited in these batch tests by the amount of oxygen which was introduced into the reactor headspace and is in the realm of concentration—limited reaction conditions.

Three batch oxidations each were conducted with Duoseal™, Hydrocount™, Ready Value™, and TCE. Apparent average reaction rate constants for Duoseal™ vacuum pump oil and the other three organic compounds were about 1 x 10—5/sec; added mechanical agitation is probably responsible for the greater oxidation rates achieved. For Duoseal™, the amount of residual organic compounds in the catalyst solution after oxidation of over 7 g of Duoseal™ for 2—3 hrs was less than that in the freshly prepared catalyst solution alone. The amount of oxygen consumed was consistent with complete oxidation, and the absolute destruction efficiency for all organic material in the reactor was 0.9996 g/g. For Hydrocount™ and Ready Value™, oxygen consumption indicated complete oxidation. Greater than 0.999999 g/g oxidation of the parent compounds, o—xylene and 1,2,4—trimethylbenzene, was achieved in 3 hrs, and the absolute destruction efficiency for all organic materials was 0.995 g/g after 3 hrs. Oxidation of TCE proved to have unexpected consequences on the reactor materials; the entrained gas stirrer head was attacked and corroded, presumably by a corrosion/erosion mechanism, because corrosion appeared only where the catalyst solution flowed rapidly past the parts. As a result, oxygen consumption indicated greater than 1.0 g/g oxidation of the TCE, with the excess oxygen undoubtedly being used as the metal parts were oxidized. A destruction efficiency of 0.9995 g/g was achieved for TCE in 3 hours, and the absolute destruction efficiency for all organic materials was 0.995 g/g. No buildup of significant amounts of unreacted byproducts was seen in any of the oxidations in the 4-L reactor.

Catalyst Solution Pressure and Composition

Of interest in the design of a prototype waste treatment unit are the pressure and composition of the catalyst solution vapors under typical operating conditions. Figure 5 gives the experimentally measured pressure versus temperature for the 4-L bench-top unit containing 1.5 L of catalyst solution and pressurized with 690 kPa oxygen. The gases in the headspace contribute some of the pressure increase with temperature, and

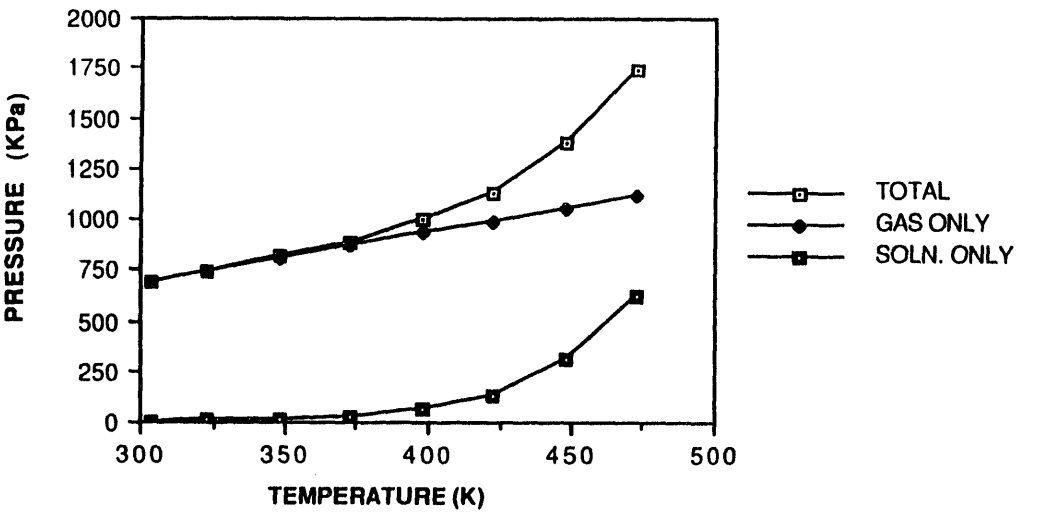

Figure 5. Pressure Vs Temperature for DETOX pressurized with 690 kPa Oxygen.

their pressure curve is shown on the graph. The difference between the total system pressure and the permanent gas pressure is the vapor pressure of the catalyst solution. Samples of the reactor vapor taken at 473 K were analyzed for water and HCl content; it was found that the vapor is approximately 6.5 g/m^3 HCl, and essentially 1.0 m3/m3 water vapor when the permanent gas volume is subtracted. The HCl content of the headspace gases was somewhat lower than expected and is thus expected to be of less concern than anticipated.

CONCLUSIONS

To date DETOX would appear to have good application to the volume reduction of low-level and mixed liquid wastes containing significant amounts of organic compounds. Reaction conditions have been identified that increase the oxidation rate for organic compounds by several orders of magnitude. The catalyst solution can solvate heavy metals and can remove organic contaminants from mineral and sorbent materials. Destruction efficiency studies have shown at least 0.999999 g/g destruction and no build-up of nonreactive by-products. Gas analysis studies have demonstrated complete oxidation to carbon dioxide. The process compares favorably with existing wet oxidation systems, in that it achieves more complete oxidation of a variety of organic compounds using an inexpensive oxidant at moderate temperature and pressure, and it can dissolve and concentrate metals, including heavy metals and metallic radionuclides. Estimates of waste processing costs (including capital costs) indicate that the process is competitive with incineration for volume reduction of mixed and low-level wastes. Results from the bench-top unit indicate that there should be no reactivity concerns in scaling the process up to larger processing volumes, as long as effective mixing can be maintained. The next phase of development will be converting the 4-L bench-top unit to a continuous processing system that can oxidize multiple gram quantities of organic compounds per hr. The continuous unit will be a test bed for prototype design concepts.

ACKNOWLEDGMENTS - We express our sincere appreciation to the United States Department of Energy for sponsoring this effort.

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MEDIATED ELECTROCHEMICAL OXIDATION OF MIXED WASTES

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ABSTRACT. The Mediated Electrochemical Oxidation process was studied for destroying low-level combustible mixed wastes at Rocky Flats Plant. Tests were performed with non-radioactive surrogate materials: Trimsol for contaminated cutting oils, and reagent-grade cellulose for contaminated cellulosic wastes. Extensive testing was carried out on Trimsol in both small laboratory-scale apparatus and on a large-scale system incorporating an industrial-size electrochemical cell. Preliminary tests were also carried out in the small-scale system with cellulose. Operating and system parameters that were studied were: use of a silver-nitric acid versus a cobalt-sulfuric acid system, effect of electrolyte temperature, effect of acid concentration, and effect of current density, Destruction and coulombic efficiencies were calculated using data obtained from continuous carbon dioxide monitors and total organic carbon analysis of electrolyte samples. For Trimsol, the best performance was achieved with the silver-nitrate system at high acid concentrations, temperatures, and current densities. Destruction efficiencies of 99% or greater, and coulombic efficiencies up to 70% were obtained. For the cellulose, high destruction efficiencies and reasonable coulombic efficiencies were obtained for both silver-nitrate and cobalt-sulfate systems.

INTRODUCTION

Mediated Electrochemical Oxidation (MEO) was originally developed for dissolution of difficult-to-dissolve forms of plutonium oxide, but later was found to be effective for oxidizing non-polymerized organic materials. Extensive development work on this technology has been done at the Pacific National Laboratory (PNL) and at the Lawrence Livermore National Laboratory (LLNL), in the United Kingdom, and in France (1-4). MEO is an inherently safe process, since the hazardous and radioactive materials are completely contained in the aqueous phase and operating temperatures and pressures of the system are low (well below 100°C and 30 psig).

The most commonly used mediator-electrolyte combination is silver in nitric acid. The process produces divalent silver ion, a strong oxidizing agent, which dissolves the radioactive components of mixed wastes and destroys the organic components. Other mediator-electrolyte combinations (e.g., cobalt in sulfuric acid, and iron and cerium in various acids) have also been investigated.

In the past, work at LLNL has focused on understanding the basic science and modeling the dissolution and destruction mechanisms. To this end, the reaction rates of water with Ag(II) were measured using spectrophotometric methods, and the diffusivity of silver ions in nitric acid was estimated using a rotating disk electrode (5). The breakdown of organics, such as ethylene glycol, was modeled in detail with the formation and eventual destruction of intermediate compounds (6-8). Dissolution of plutonium oxide was also modeled and system studies were conducted to optimize system operating parameters (9,10). Also, a full-scale system was built for plutonium oxide dissolution and tested with surrogate materials (11).

Recently, the effort has been directed toward studying the destruction of combustible Rocky Flats mixed wastes, specifically, wastes containing Trimsol and cellulosic material. Although a major part of the work involved small-scale laboratory apparatus, it was important to demonstrate destruction on large industrial-scale equipment so results could be confidently extrapolated to plant-sized operations. Also, since Trimsol contains chlorinated organics, and silver is precipitated by chlorides, an additional recovery step is needed. Hence, an alternate mediator, cobalt, was tested. Cobalt also has the advantage that it may be possible to use it in undivided cells, and its removal from sulfuric acid has been demonstrated at the University of California at Los Angeles down to 2-ppm levels. Therefore, cobalt was also used for testing the destruction of cellulosic materials.

EXPERIMENTAL WORK

The experimental work on organic destruction was conducted in two phases. In the first phase, small laboratory-scale experiments that were carried out where it was relatively easy to vary system temperature, acid concentration, and mediator-electrolyte combination. The experiments were conducted with Trimsol as a surrogate for the low-level mixed waste oils at the Rocky Flats Plant. Preliminary testing of cellulosic wastes was also carried out using reagent-grade cellulose. In all small-scale experiments, a measured amount of organic material was introduced into the anolyte prior to turning on the cell. That is, the test was run in a batch feed mode. In the second phase, organic destruction was demonstrated in a bench-scale system using a commercially available industrial-size cell. Experiments were performed on this system with Trimsol at different acid concentrations and temperatures. In these experiments, the organic was fed and metered continuously to the anolyte during the run. The experiments are described in more detail below.

Small-Scale Experiments with Trimsol

Small-scale experiments were performed in H-shaped cells which could be fitted with an ion-selective membrane separating the two cell compartments. In most of the experiments conducted for organic destruction, the cell was placed in a closed container and the gas within was continuously sampled for carbon dioxide using a Horiba Model 2000 Infrared Gas Analyzer. With this technique, it is possible to determine the instantaneous generation rate of carbon dioxide, which is the desired end-product in the oxidation of organic carbon. A schematic of the setup is shown in Fig 1. Details of the container and the H-cell are shown in Fig 2. One compartment of the cell was fitted with a rotating platinum cylinder for the anode, while the other contained a platinum strip for the cathode. At the end of the experiments, samples of the catholyte and anolyte were removed and sent for total organic carbon (TOC) analysis. Experiments with Trimsol, using the continuous carbon dioxide monitor, were performed at different conditions to determine the effect of various system and operational parameters. The parameters studied and their ranges were as follows:

- mediator-acid combination — silver-nitric acid and cobalt-sulfuric acid
- acid concentration — 4 to 10 M for nitric acid; 1.67 to 6 M for sulfuric acid
- cell current — 673 to 1020 mA
- electrolyte temperature — 20 to 70°C

Small-Scale Experiments with Cellulose

Experiments in a small H-cell were conducted with reagent-grade cellulose, using the continuous carbon dioxide monitoring system described above. The parameters studied here were the mediator-acid combination, acid concentration, and electrolyte temperature. The range of parameters was similar to that listed above for Trimsol.

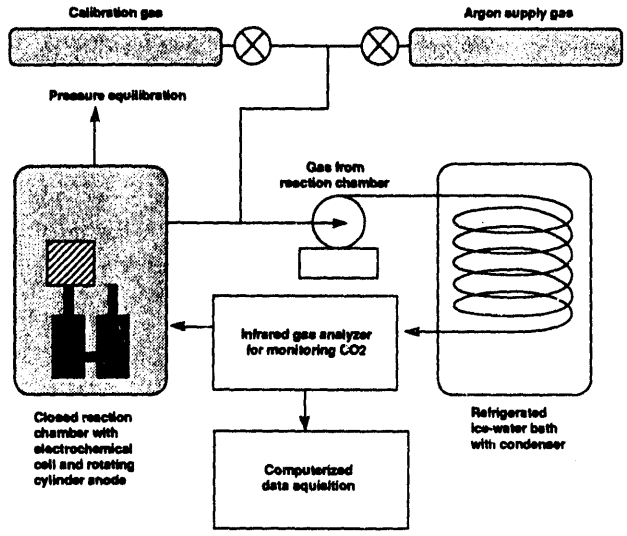

Figure 1. Schematic of small-scale apparatus in closed container with carbon dioxide monitor.

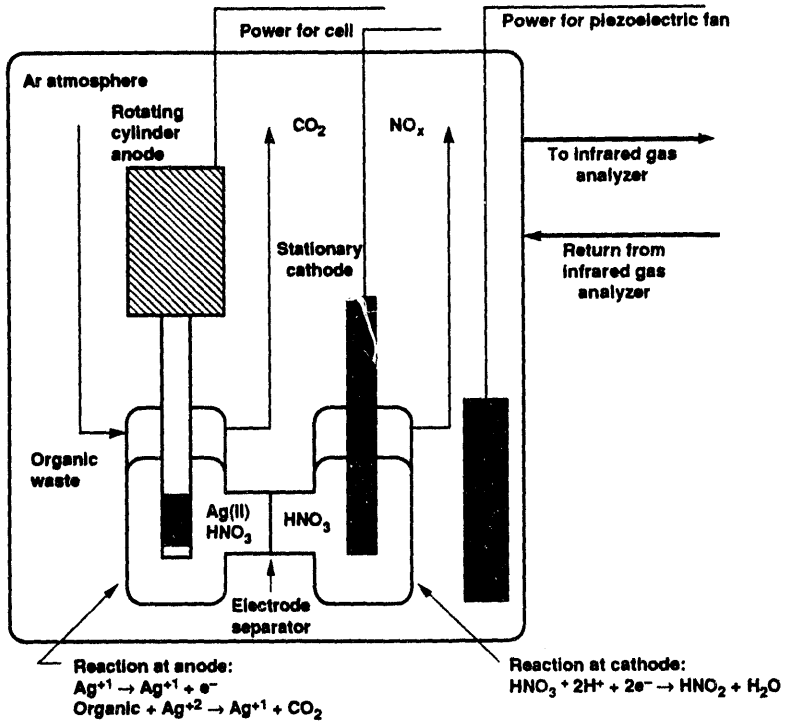

Figure 2. Schematic of closed container and H-cell

Large-Scale Experiments with Trimsol

The large-scale system was built with a commercially available industrial electrochemical cell, called the FM-21, built by Imperial Chemical Industries (ICI). The cell has a plate-and-frame design, with expanded metal electrodes and turbulence promoters installed on the anodes. The electrodes are made of niobium with the anodes coated with platinum. The cell stack presently has two anodes and three cathodes, with a capacity to expand to accommodate several more electrode pairs. The anode and cathode compartments are divided by cation-selective membranes (Nafion 117). The present system has the capacity of delivering up to 3000 A of limiting current to the mediator.

A schematic of the flow system is shown in Fig. 3. Included in the figure are auxiliary carbon dioxide monitoring, gas scrubbing and acid regeneration systems, which have not yet been installed and are part of a future upgrade. In the experiments with Trimsol, the oil was continuously fed to the anolyte just downstream of the reservoir. Samples were taken periodically from the anolyte throughout the runs, and from the catholyte at the end of the runs, for post-test TOC analysis. Experiments were conducted only with the silver-nitric acid system. The experimental parameters studied were acid concentration (4 to 10 M) and electrolyte temperature (25 to 70°C).

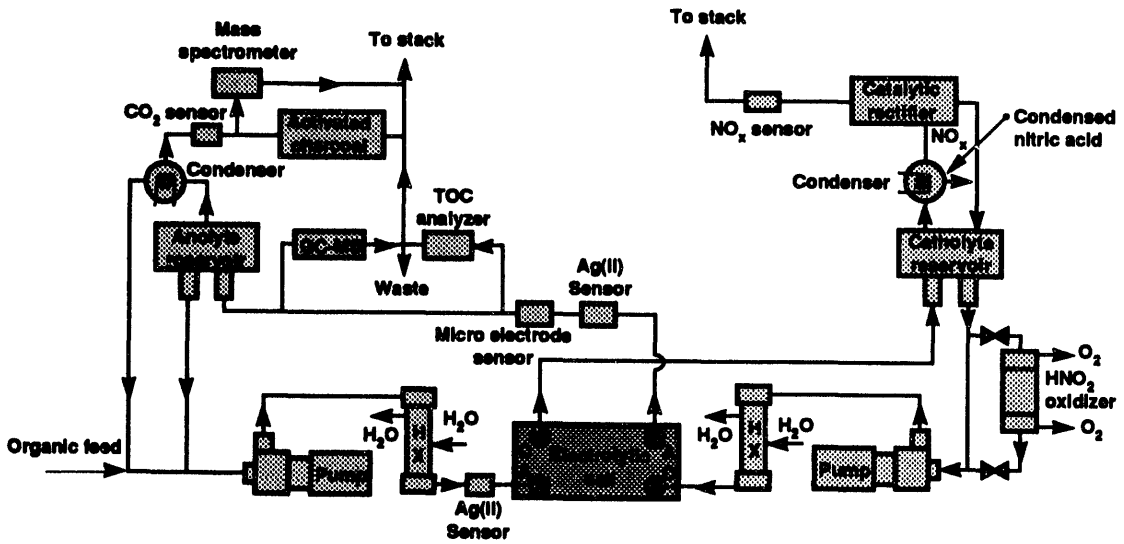

Figure 3. Schematic of the large-scale MEO system.

RESULTS AND DISCUSSION

The results of the Trimsol and cellulose destruction experiments are discussed separately below.

Trimsol Results

Trimsol is a mixture of various heavy oils, chlorinated hydrocarbons and other organics. A pseudo-chemical formula for Trimsol, neglecting the small amounts of sulfur and nitrogen present, is $C_{5.69}H_{10.71}O_{0.47}Cl_{0.31}$, where it is understood that the subscripts refer to moles of each element per 100 g of Trimsol. The number of Ag(II) ions required to completely destroy 100 g of Trimsol is then given by

$$C_{5.69}H_{10.71}O_{0.47}Cl_{0.31} + 10.91H_2O + 32.22Ag^{++} \longrightarrow 32.22Ag^{+} + 32.53H^{+} + 5.69CO_2 + 0.31Cl^{-} \qquad (1)$$

Hence, 5.69 moles of carbon dioxide are generated and 32.22 moles of electrons must be removed at the anode when 100 g of Trimsol are completely oxidized. The corresponding water generation occurs in the cathode compartment. Note that the chlorine ions will combine with Ag(I) to precipitate out as insoluble silver chloride from the solution.

In the small-scale experiments with Trimsol, where carbon dioxide evolution is continuously measured, it is possible from Equation (1) to determine the destruction efficiency with time from the percentage of organic carbon converted to carbon dioxide. The coulombic efficiency can also be determined by comparing the amount of charge delivered up to the time of complete destruction with the amount theoretically required from Equation (1). The final destruction efficiency can also be determined from TOC analysis of the post-test samples.

The results from the small-scale tests showed that coulombic and destruction efficiencies increased as the mediator-acid combination was changed from cobalt-sulfuric acid to silver-nitric acid, and as the current increased. The efficiencies increased dramatically when the concentration of nitric acid is increased. For all runs at the higher concentration of nitric acid, irrespective of temperature, the destruction efficiencies were high—in the 98–99+ range. The coulombic efficiency, however, showed a marked dependence on temperature, increasing from about 20% at 20°C up to 70% at 70°C.

The results from the large-scale system, in general, were similar to those from the small scale-system. At low acid concentrations (4 M) and low temperatures (25°C) a build up of waxy material was observed floating at the top of the anolyte reservoir. The various oils in Trimsol are kept emulsified by surfactants, which are immediately attacked by the acid. The oil droplets then begin to coalesce and the reduced available surface area slows down further attack by the mediator. However, the problem of separation did not appear at higher acid concentrations and higher temperatures. A reason for this may be that higher oxidation rates, corresponding to higher temperatures and acid concentrations, result in the destruction of oil droplets before they have a chance to coalesce. At the highest acid concentrations (10 M) and temperatures (70°C) tested, destruction efficiencies of over 99% and coulombic efficiencies of 70% were achieved. Higher coulombic efficiencies are possible but at the expense of a decrease in destruction efficiency.

It should be noted that for both the small rotating anode and the large expanded metal electrodes, the limiting current was calculated, and the cell current in these experiments was always maintained well below the limiting current. Hence, coulombic inefficiencies are due to slow reaction kinetics (especially slow surface kinetics for insoluble organic components) and parasitic parallel bulk reactions, rather than inefficiencies resulting from oxidation of water at the anode.

Cellulose Results

Cellulose is a straight-chain carbohydrate with a chemical formula $(C_6H_{10}O_5)_x$. The repeating unit, $C_6H_{10}O_5$, has a molecular weight of 162 g/mole, and the amount of Ag(II) required to completely oxidize it is given by

$$C_6H_{10}O_5 + 7H_2O + 24Ag^{++} \longrightarrow 24Ag^{+} + 24H^{+} + 6CO_2 \qquad (2)$$

Hence, the complete destruction of 162 g of cellulose will require 24 moles of Ag(II), which will be generated by 24 moles of electrons removed from the anode. During this process, six moles of carbon dioxide will be released.

In the small-scale experiments with cellulose, the carbon dioxide evolution was continuously measured. From Equation (2), the instantaneous destruction efficiency can be calculated from the percentage of organic carbon converted to carbon dioxide. The coulombic efficiency can be calculated by comparing the theoretical charge required, to produce the carbon dioxide generated, to the actual charge delivered. The results showed that coulombic efficiencies up to 80% and destruction efficiencies close to 100% can be obtained with both cobalt-sulfuric acid and silver-nitric acid systems at higher acid concentrations and electrolyte temperatures of 50°C and above.

CONCLUSIONS

The MEO process is capable of achieving high destruction efficiencies and reasonable coulombic efficiencies for both Trimsol and cellulose. For Trimsol, the tests show that high currents, acid concentrations, and temperatures enhance the destruction efficiencies. The silver-nitric acid combination is preferred since it is a more powerful oxidizing system than cobalt in sulfuric acid. Since Trimsol is composed of many insoluble oils kept in emulsion by surfactants, which break down in acids, the oil has a strong tendency to coagulate and separate out from the electrolyte. Hence, it is important to have a highly oxidizing environment when Trimsol is fed into the electrolyte so the destruction processes have a chance to attack the large initial surface area available before the droplets start to coalesce. Cellulose, on the other hand, does not coalesce and appears to break down easily, thus allowing the use of less powerful oxidizing agents.

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TREATMENT OF A SIMULATED MIXED WASTE WITH SUPERCRITICAL WATER OXIDATION

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ABSTRACT. This report describes a series of tests using supercritical water oxidation (SCWO) to process cutting oil containing a simulated radionuclide. The goal of the tests was to evaluate the technology's ability to process a highly chlorinated waste representative of many mixed waste streams generated in the U.S. Department of Energy complex. The testing was conducted with a bench-scale SCWO system developed by the Modell Development Corporation. Significant test objectives included process optimization for adequate destruction efficiency, tracking the radionuclide simulant and certain metals in the effluent streams, and assessment of reactor material degradation resulting from processing a highly chlorinated waste. Test results have been summarized from laboratory analysis of the liquid effluent, and of the solid effluent, and witness wire data for corrosion and deposition evaluation.

INTRODUCTION

This work was initiated at the Idaho National Engineering Laboratory (INEL) to answer some basic questions about the Supercritical Water Oxidation (SCWO) process. SCWO research has been conducted for some time, but experimental data generated from existing SCWO technology has not been widely disseminated. Fundamental property data for mixtures of water and organics at conditions at and above the critical point of water are also scarce. Many researchers have responded to the need for SCWO research by recommendation that significant energy be applied towards explaining or attempting to explain the fundamental science of supercritical water oxidation, particularly in the area of chemical kinetics (1). The science of supercritical water oxidation remains fertile ground for speculation and research and will one day reap benefits in predictive capability. The complexity of this science, however, including the chemistry of SCWO and the changing properties of organic/water mixtures at SCWO conditions, makes one realize that progress in these fundamental areas will be slow. Combustion designers have demonstrated that technological advances must often precede basic understanding of the science of combustion. This approach led to the successful development of gas turbines for air and land-based applications, and should likewise prove viable in SCWO technology development for waste treatment.

Our focus for the tests described in this paper was to shed some light on the limits and potential of existing SCWO technology by generating data that would reflect the state of the art relative to waste destruction, composition of the effluent, and corrosion and deposition resulting from processing a challenging waste relevant to the U.S. Department of Energy (DOE). The waste stream, TRIM®SOL Surrogate, was used to represent a large volume, halogenated mixed waste stream located at the Rocky Flats Plant. Four test series were completed with the Modell Development Corporation (MODEC) SCWO process in Framingham, Massachusetts. The first two series were for establishing baseline data, and for optimizing SCWO operating conditions for the TRIM®SOL mixture. The last two runs were used to collect the majority of effluent data and to collect corrosion and deposition data with witness wires.

The DOE is evaluating SCWO technology to determine if it could be used in the future for treatment of DOE mixed waste. The INEL SCWO Program was initiated to pursue this goal. The testing described in this report was conducted under this SCWO program and was designed to meet the following objectives:

- To evaluate existing SCWO technology on its ability to treat a simulated mixed waste
- To assess corrosion and deposition effects in the SCWO reactor
- To track the disposition of a simulated radionuclide in the effluent streams to gain preliminary information on plutonium disposition in SCWO treatment.

Supercritical water oxidation is an environmentally acceptable alternative for treatment of organic wastes. With residence times in the order of seconds to several minutes, oxidation efficiencies greater that 99% can be achieved. Above its critical point water becomes an extremely good solvent for organic materials which are readily oxidized in the presence of air or oxygen. SCWO technology takes advantage of this by bringing organics and water to a temperature and pressure above the critical point of water and allowing complete oxidation of the organics. The SCWO process converts organic materials to carbon dioxide and inorganic acids (2). It produces solid, liquid, and gaseous effluents. SCWO differs from incineration because it operates at mild temperatures (400 to 650°C) and high pressures (24 to 28 MPa) in a much more controlled environment.

The INEL has been involved with private sector development of SCWO technology through DOE Cooperative Agreements including work with MODEC. The MODEC reactor used for this work has a total throughput of approximately 115 L/day (waste and water). MODEC engineers operated the SCWO system in Framingham, Mass. during the five weeks of testing, with oversight and assistance from EG&G Idaho engineers.

DESCRIPTION OF EXPERIMENTS

A full description of the MODEC SCWO system and some operating conditions is not included in this paper since much of this technology is considered proprietary. Several reviews have been published describing non-proprietary aspects of existing SCWO systems (3-6,8). The MODEC SCWO process can be broadly divided into the following sections:

- Waste feed and pressurization
- Oxidizer feed and pressurization
- Reactor, including pre-heat, reaction, and cool-down sections
- Solids/Liquid/Gas separator system
- External heat input

The SCWO tests were run with one simulated waste feed in varying concentrations. This waste was chosen to simulate a mixed waste stream called Fluidized Bed Unit oil, that is currently in the Rocky Flats inventory. This oil consists primarily of a cutting oil, TRIM®SOL, manufactured by the Master Chemical Company. This waste is a high priority mixed waste in the DOE system, i.e. viable treatment options for this waste need to be identified to comply with regulatory requirements. It was also selected as a good candidate because it is a highly chlorinated waste, representing many mixed waste streams in the DOE inventory. It was anticipated that processing a highly chlorinated waste would also provide valuable data on corrosion effects in the SCWO system. The waste used for most of these tests was called a TRIM®SOL Surrogate because it had metals and a radionuclide surrogate added to it to simulate the Rocky Flats mixed waste stream. The TRIM® SOL Surrogate consisted of the specified concentration of TRIM®SOL in water and 200 ppm zinc sulfate, 180 ppm lead chloride, and 280 ppm cerium chloride as the radionuclide

simulant. The concentration of the TRIM®SOL in the mixture was varied from 1% to 3.75%. Four test series were defined as follows:

- Test 1 - Baseline and System Calibration.
- Test 2 - Optimize operating conditions using TRIM®SOL and water only.
- Test 3 - Process TRIM®SOL Surrogate for liquid/solid samples.
- Test 4 - Process TRIM®SOL Surrogate with witness wires for corrosion data.

The goal of the Test 2 series was to find optimum operating conditions for processing TRIM®SOL, including adequate destruction efficiency, and the highest concentration in water that could be processed without measurable corrosion. Nickel and chrome levels in the liquid effluent were monitored during processing to assess possible corrosion increase.

Test 3 runs were done with the 3.75% TRIM®SOL Surrogate. One goal of these tests was to collect a large enough solids sample for a Toxicity Characteristic Leaching Procedure (TCLP) test, that is, greater than 10 grams of solids. All Test 3 runs used the optimum conditions determined from Test 2. The Surrogate was used to determine what happened to the metals and the radionuclide simulant after SCWO processing.

For the Test 4 runs the 3.75% concentration TRIM®SOL Surrogate was used. These tests were done to generate data on corrosion for a sufficient duration to obtain measureable rates. The operating conditions used in Test 3 were maintained for all Test 4 runs. The corrosion measurements were done with Inconel 625 witness wires. Three witness wires were installed throughout all sections of the SCWO reactor. All three wires were pre-treated in the reactor as a corrosion prevention measure prior to starting Test 4. One wire was removed after pre-treatment to use as a baseline. Test 4 runs were done for approximately 20 hrs duration over several 5 to 10 hr intervals before the second witness wire was removed. The third witness wire was removed after 18.5 additional hrs of operation so that the last wire had a total of 38.5 hours of exposure. Some cleaning procedures were completed during Test 4 to reduce deposition and prevent plugging in the reactor during processing.

Sampling Activities

Sampling was conducted throughout these tests to obtain information on the waste feed and the different effluent streams. The sampling activities were defined for the following streams:

- Liquid waste feed
- Liquid effluent
- Gaseous effluent
- Solids effluent

Samples on the liquid waste feed were sent to an off-site laboratory for analysis certified to U.S. Environmental Protection Agency (EPA) standards. Liquid effluent samples were also sent off-site for EPA certified analysis. Composite samples are a combination of liquid samples taken over the entire duration of the test to represent an average effluent composition. The composite samples do not include liquid from a transition period. A transition period for these tests is defined as thirty minutes after changing a critical operating parameter.

The gaseous effluent samples were measured and recorded with on-line gas chromatography equipment. Each time gas measurements were conducted a sample was taken from the gas exiting from various points in the SCWO separator system. All samples represented the final condition of the off-gas as it goes into the stack. Analysis of these samples was used to monitor the stack gas.

The solids were separated from the liquid effluent for some samples, and were also taken from different cleaning procedures that removed some deposits from the reactor. Solids samples were sent off-site for compositional analysis and for TCLP analysis. The TCLP sample from Test 3 was a composite of solids from all procedures. The TCLP results for Test 4 are derived from samples of solids collected from the different solids collection procedures and analyzed separately.

Witness Wire Installation and Removal

The witness wires were Inconel 625 wire and used only during Test 4. Three wires were pushed through all sections of the reactor, from the point where the feed streams enter the reactor to the last valve in the cooldown section before the separator system. The wires were not attached to anything on either end and remained free floating throughout testing. After testing each wire was pulled from the reactor manually. The first wire came out of the reactor in one length. The second wire came out in two pieces, with the second piece a three foot section on the end of the cooldown section. The third wire, with 38.5 hours of processing exposure, came out in several pieces. The wire was broken at one point in the pre-heat section and showed heavy corrosion and deposits. Another break occurred at the cooldown section but was not as visibly corroded. The last piece of this wire was recovered but not used as data because its orientation in the reactor was not clear after its removal from the reactor.

TEST RESULTS

Effluent Analysis

The composition of the liquid effluent for Test 3 is shown in Table 1. These results are from composite samples from the test series. Compositional results of laboratory analysis of Test 3 solids samples are also tabulated in Table 1. The solids analysis was completed from a composite of all solids collected from Test 3, including solids from deposits collected from inside the reactor. Gaseous effluent data were not comprehensive enough for comparison with other effluent streams. Complete feed and effluent mass balances could not be calculated due to lack of comprehensive gaseous effluent data.

TCLP Results

The TCLP test estimates how much a metal will leach out of the solids over time, and is meant for judging whether the solids can be safely landfilled or not. TCLP tests were completed on some solids effluent samples taken from Test 3 and from Test 4. The laboratory results are shown in Table 2. The TCLP results show only the portion of metal from the sample that leaches, therefore, these masses are not used for mass balance calculations. The liquid feed column shows the amount of metal added to the feed, not the amount measured in feed samples. The steady state results for Test 3 and 4 represents solids separated from the liquid effluent stream.

Mass Balances

Three compounds were added to the TRIM®SOL to make the surrogate used in Test 3 and Test 4. These were used to track the path of the metals, zinc, lead, and cerium, from the reactor through the separators, and to determine their fate as a result of SCWO processing. Mass balances were performed on these three metals for this purpose. Due to limited data for the gaseous effluent comprehensive mass balance calculations could not be completed. The mass of each metal going in was calculated from the known quantity of the compound placed in the feed, which translated into a weight percent of the metallic element for the TRIM®SOL Surrogate batches used as the feed in Test 3 and in Test 4. These expected masses were then compared to actual masses of each metal measured in the solids effluent collected from Test 3 and Test 4.

Table 1 Liquid and solid effluent composition.

	Test 3 Feed	Test 3 Liquid Effluent	Test 3 Solids Effluent
Mass (grams)	~40000	32220	14.06
pH	6.9	1.3	--
Total Solids (ppm)	96400	254	--
Cl_2(ppm)	220	4580	--
SO_4(ppm)	4390	32.00	--
K (ppm)	71.40	5.79	1960
Na (ppm)	195	19.50	4460
Cr (ppm)	ND[a]	5.54	15200
Ni (ppm)	ND	8.60	206000
Mo (ppm)	ND	6.52	9350
Fe (ppm)	0.50	1.37	8040
Zn (ppm)	4.45	16.20	14200
Ce (ppm)	154	ND	11600
Pb (ppm)	12.00	23.30	73200
TOX[b] (ppm)	2.460	3.870	--
TOC[c] (ppm)	34600	11	--

[a]ND means Not Deteced.
[b]TOX = toal organic halides
[c]TOC = total organic carbon

Table 2. TCLP results.

Metal	Liquid Feed (Tests 3 & 4) (ppm)	Test 3 TCLP Steady State (ppm)	Test 4 TCLP Steady State (ppm)	Test 4 TCLP Deposited solids, sample A (ppm)	Test 4 TCLP Deposited solids, sample B (ppm)
Zinc	77	130	126	206	54.8
Cerium	149	186	56.5	227	59.5
Lead[a]	127	74.1	56.3	84.4	75.9

[a] The current EPA TCLP Standard for lead is 5.0 ppm.

The mass balance results were as follows:

Test 3:	Actual Mass (grams)	Predicted Mass (grams)	Percent in Effluent
Zinc	0.85	3.24	26.3
Cerium	1.63	6.60	24.7
Lead	1.96	5.36	36.6

Test 4:	Actual Mass	Predicted Mass	Percent in Effluent
Zinc	2.79	11.08	25.2
Cerium	4.84	22.57	21.4
Lead	9.07	18.33	49.5

The most obvious result of these mass balances is that much of the metal mass has not been accounted for. This is consistent with results of related work (6,7). There are several likely possibilities for the fate of the missing masses. Some mass, possibly a few percent, would be lost from volatilization during compositional analysis. It could be speculated that some metal mass was lost through volatilization into the SCWO gaseous effluent, although this seems highly unlikely for the metals under consideration. The most likely fate for these metals is that they remained deposited on the SCWO reactor walls. Microscopic analysis of the witness wires showed the consistent presence of cerium, zinc, and lead on the wire surfaces. Quantitative data on these deposits could not be obtained, but there is little doubt that the amount of metals missing from the solids effluent could be deposited throughout the reactor walls in a manner similar to the deposition observed along the witness wire lengths. The deposits found on the witness wires were often located in areas of corrosion where base metal loss was severe. The MODEC SCWO process includes a means for maintaining the flow area inside the reactor. The co-location of deposition and corrosion could explain why metal masses could be remaining in the reactor without appreciably changing the flow area inside the reactor.

Destruction/Removal Efficiency Calculations

One parameter representing the effectiveness of the SCWO process is the Destruction/Removal Efficiency (DRE). For analysis of the benchscale tests this parameter is defined as:

$$DRE = \{1 - \frac{(\text{Effluent TOC})}{(\text{Influent TOC})}\} X\ 100 \qquad (1)$$

DRE was calculated using analysis results for Total Organic Carbon (TOC) from the waste feed and liquid effluent only. The DRE results for all tests are tabulated in Table 3.

Corrosion/Deposition Analysis

The witness wire sections were examined by INEL metallurgists using metallographic analysis and Scanning Electron Microscopy (SEM). Metallographic analysis resulted in estimates of corrosion rates for the wires in the SCWO environment in mils per year. Gravimetric (weight loss) methods were not used to determine the corrosion rate because it was not feasible to place small corrosion coupons inside the reactor sections for these tests, and because anticipated scaling on coupons might alter the data. As an alternative, the diameters of the witness wires were measured using the metallograph.

Table 3. Destruction/removal efficiency results.

Test Number	TOC (ppm)	DRE
Test 2.1 Feed	6440	
Test 2.1 Effluent	12.2	99.8106
Test 2.2 Feed	16400	
Test 2.2 Effluent	29.6	99.8195
Test 2.3 Feed	33900	
Test 2.3 Effluent	232	99.3156
Test 2.4 Feed	29100	
Test 2.4 Effluent	76.3	99.7378
Test 2.5 Feed	27300	
Test 2.5 Effluent	ND<1	>99.9963
Test 2.6 Feed	28500	
Test 2.6 Effluent	ND<1	>99.9965
Test 3* Feed	34600	
Test 3* Effluent	11	99.9682
Test 4* Feed	28100	
Test 4* Effluent	1.28	99.9954

*These samples were composites for the entire test series.

The nominal thickness of the original witness wires before processing was 0.0625 in. Measurements of the diameter of the first wire at 68 locations along its length gave a mean value of 0.0612 in. The standard deviation for diameter was 0.0003 in, therefore, the 95% confidence interval for the true mean diameter was from 0.0606 in to 0.0618 in.

The calculated confidence interval when using mils per year is equivalent to +/- 70 mils/yr. Corrosion rates of less than 70 mils/yr could easily be attributed to measurement errors and variations in the wire diameter, not actual corrosion loss.

Figures 1 and 2 show these corrosion rates, along with the temperature profile in the three reactor sections. Figures 3,4, and 5 show original wire diameter after 20 hr and 40 hr exposure respectively. In some areas the corroded wires were irregularly shaped indicating localized corrosion (Fig. 6,7, and 8). The corrosion rates seemed to be effected by deposits that formed on the wires. These deposits seemed to form a protective coating and hence slow down the corrosion. Apparently, corrosion would occur in a specific area then layers of scale would begin to form on the wires. The corrosion would slow (or stop) until the scale spalled off. This would explain why, in general, the corrosion rates for the wire exposed to the reactor for 20 hrs were higher than the wire exposed for 40 hrs. This cyclic process could have been influenced by the procedure of testing, namely, processing in several hour shifts with shutdowns between shifts.

Most of the areas of the wires experienced general corrosion. Some areas of the wires experienced intergranular attack (Fig. 9-12). The degree of intergranular attack varied within short distances along the wires. This variance would indicate different chemical environments within short distances along the reactor. The pre-treatment process used for these tests appear to have enhanced corrosion, hence, the results may show greater corrosion than if the pre-treatment had not been used. Further testing would be needed to verify this.

The chemical composition of the deposits were analyzed using Energy Dispersive X-ray Spectrometry of the SEM. Twenty six different spectra were run on six samples at three different locations. In general, the deposits included oxides of the elements that compose Inconel 625. In addition to these oxides, cerium, zinc, lead, chloride, and sulfur were found in the deposits. Cerium and lead were mostly concentrated in the pre-heat section, with small amounts also located in the cool-down section. Zinc was detected in the cooldown section only. Chloride was detected in all areas.

CONCLUSIONS AND RECOMMENDATIONS

These conclusions are based on our observation of the MODEC SCWO system during testing, and on analysis of the test results. The testing supported our perception that the key technical problems associated with SCWO design and operation are corrosion and deposition. The data generated during these tests illustrate the extent of these problems. The data also identify specific areas where SCWO technology development should be focused, and possible paths for this development.

The results for evaluating waste destruction from SCWO were consistently positive. The MODEC SCWO process could be controlled to produce high destruction/removal efficiency (>99.9%) of a halogenated waste. The destruction/removal efficiency for these tests was calculated from the waste feed and the liquid effluent composition. Data from the gaseous effluent was not adequate for including in the destruction/removal efficiency calculations for these tests, although this is recommended for future SCWO tests.

Many DOE mixed wastes considered candidates for SCWO contain Resource Conservation and Recovery Act (RCRA) hazardous organics and inorganics. Adequate destruction efficiency of the organic constituents is one obvious objective for SCWO, but the status of what is left in the SCWO effluent is also significant. TCLP results indicate that if the waste contains high levels of hazardous metals, the solids collected from SCWO processing of this waste will probably not pass a TCLP test. This will restrict the disposal of these solids since they cannot be legally landfilled without passing the TCLP test if they are RCRA hazardous metals. There has been a perception that wastes with hazardous metals can be processed with SCWO such that the solids effluent can be land disposed (4). This may be true in the case of wastes containing very small quantities of RCRA hazardous metals. In the case of many DOE wastes, however, the metals content will be as high as that of the TRIM®SOL Surrogate, and our data indicates that SCWO processing will result in RCRA hazardous solids that cannot be landfilled, or in the case of mixed waste will still contain the radiological hazard and the hazard due to the presence of RCRA regulated metal. This means there will be some mixed waste resulting from SCWO processing of mixed waste feeds containing large quantities of RCRA hazardous metals, although the volume of mixed waste resulting from SCWO processing should be very small compared to the original waste volume. The compositional results were used to calculate destruction efficiency and to conduct mass balances on the three metals added to the TRIM®SOL surrogate. The liquid effluent contained small amounts of the metals, whereas the majority of the metals were in the solids effluent. Mass balances showed poor recovery of the three metals. The most obvious possibility for the fate of these metals was that they were deposited on the reactor walls. Scanning Electron Microscopy SEM analysis was used to evaluate the composition of deposits on the witness wires. Cerium, lead, and zinc were found in these deposits, indicating that a large portion of these metals probably remained on the reactor walls after processing. This indicates a tenacious deposition or scaling problem that must be addressed in SCWO technology development.

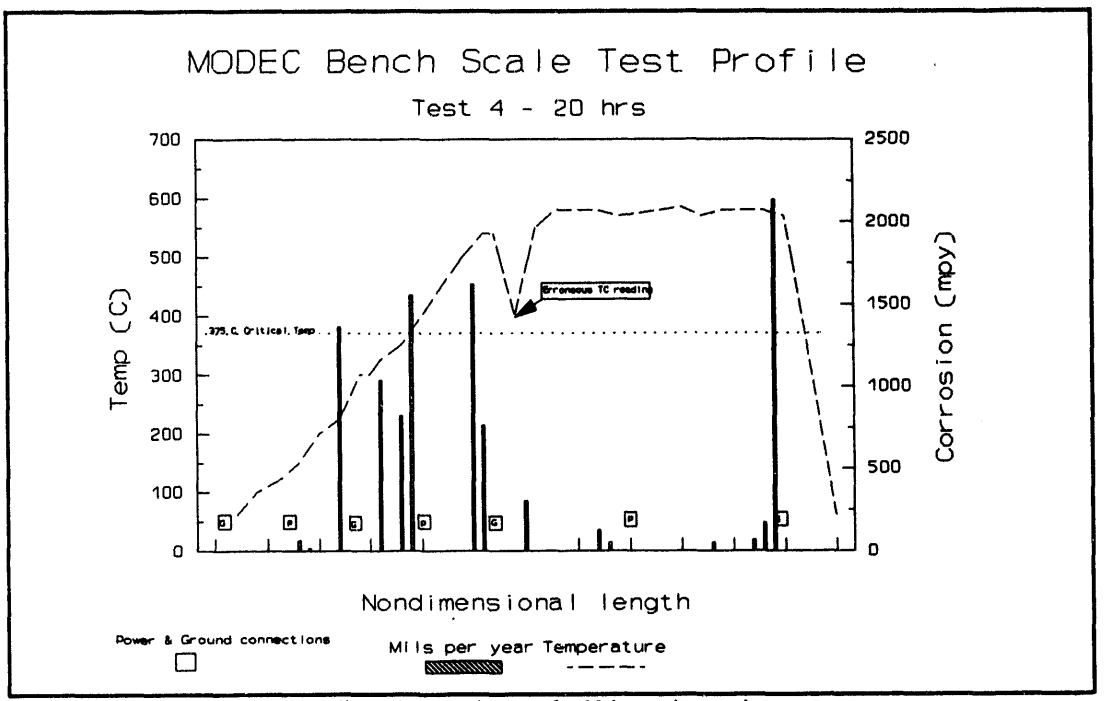

Figure 1. Corrosion rate for 20 hour witness wire.

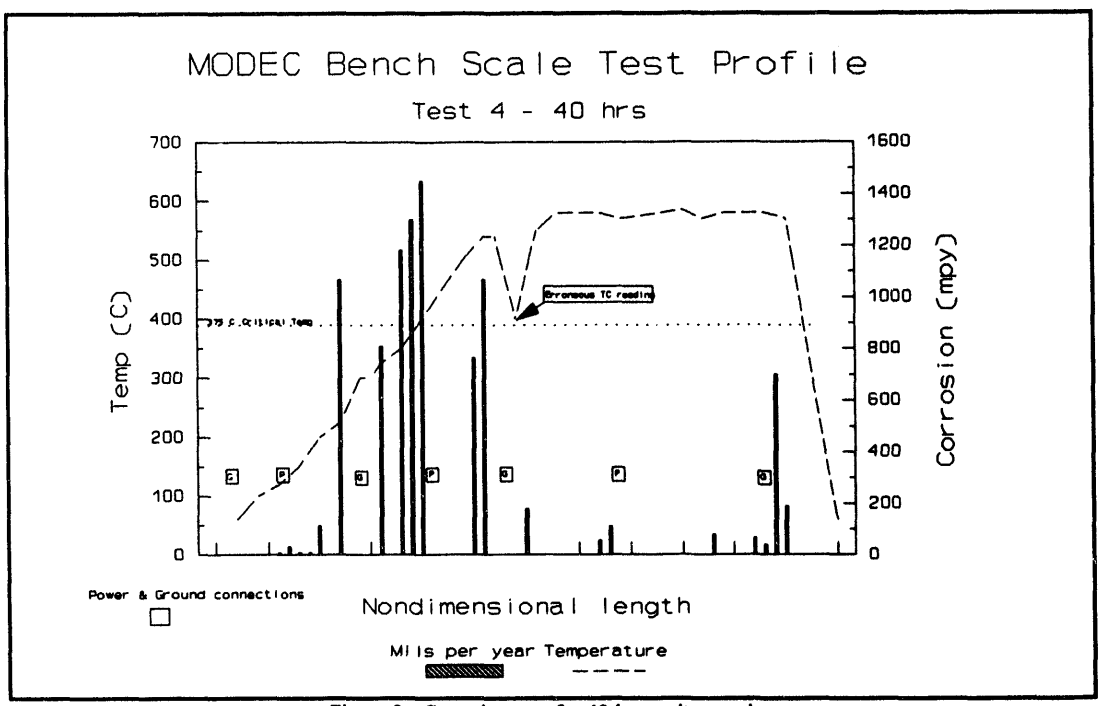

Figure 2. Corrosion rate for 40 hour witness wire.

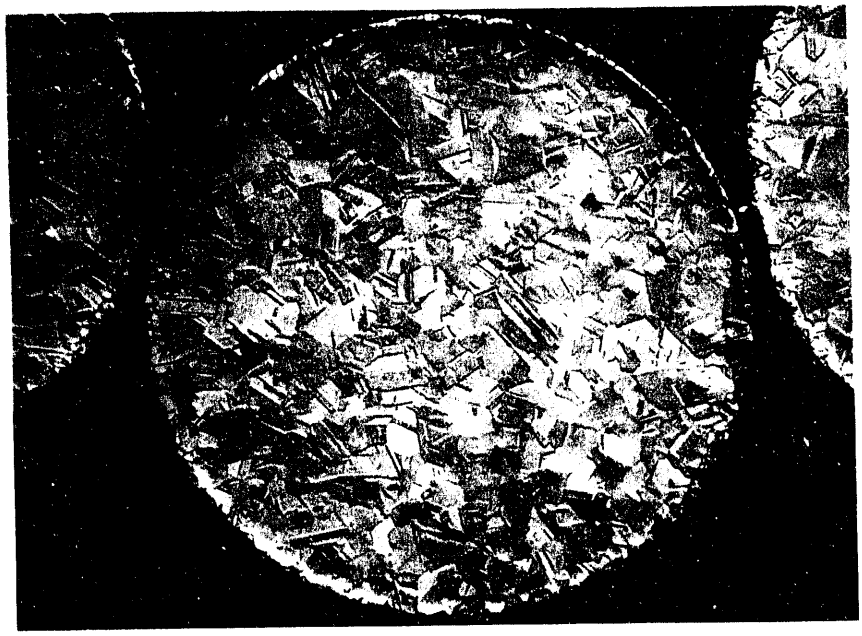

Figure 3. Original diameter of witness wire in pre-heat section (50X as polished).

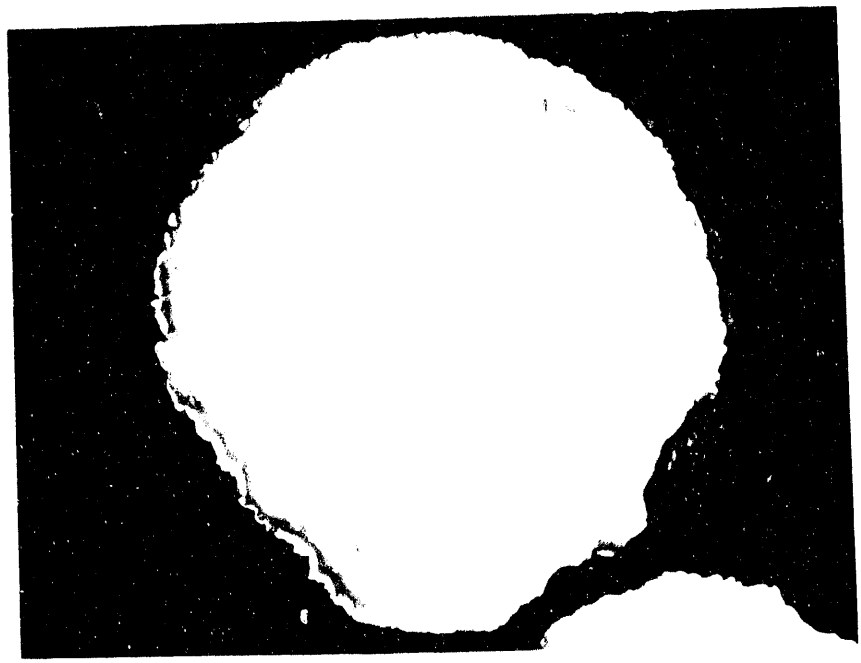

Figure 4. Wire diameter after 20 hours exposure in pre-heat section (50X as polished).

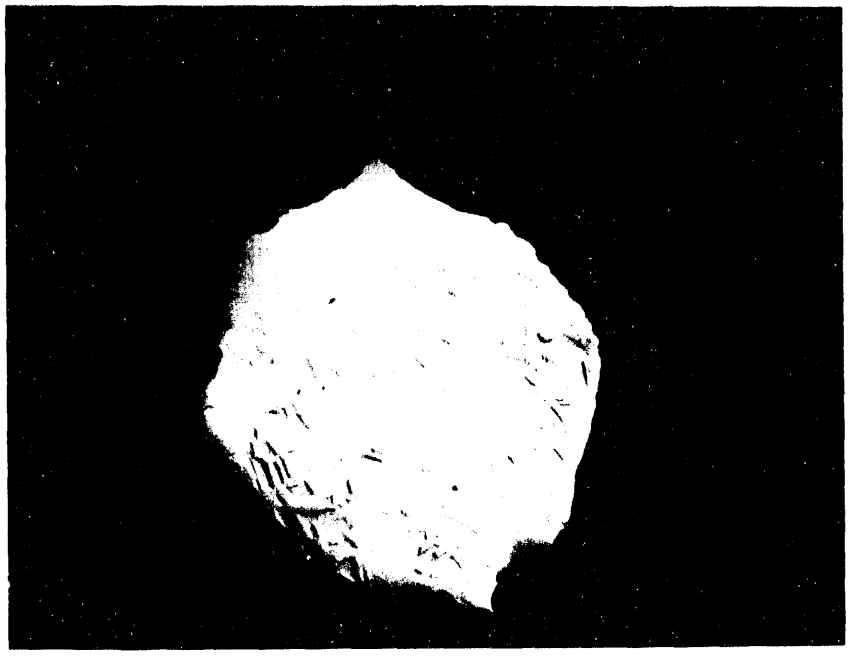

Figure 5. Wire diameter after 40 hours exposure in pre-heat section (50X as polished).

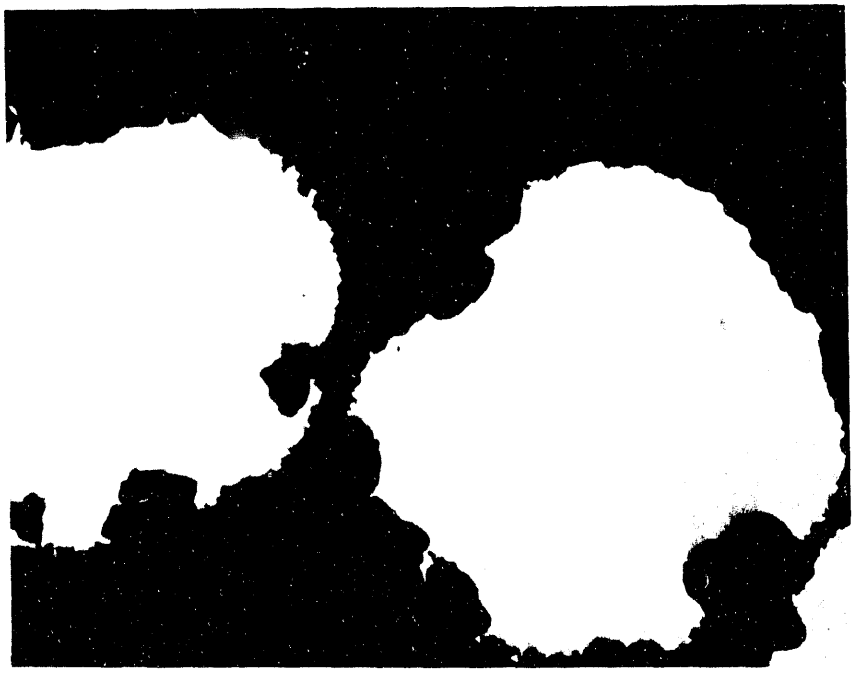

Figure 6. Irregular wire diameter after 20 hours exposure in cooldown section (50X as polished).

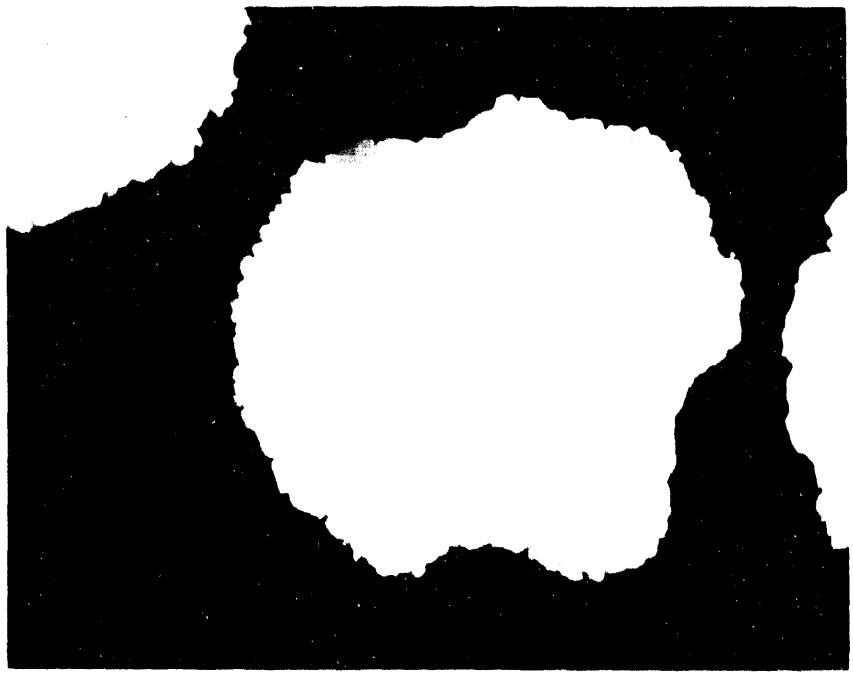

Figure 7. Irregular wire diameter after 40 hours exposure in pre-heat section (50X as polished).

Figure 8. Scale deposit on wire after 40 hours exposure in the pre-heat section (400X as polished).

Figure 9. Intergranular attack after 20 hours exposure in the cooldown section (400X as polished).

Figure 10. Intergranular attack of wires after 40 hours exposure in the pre-heat section (400X as polished).

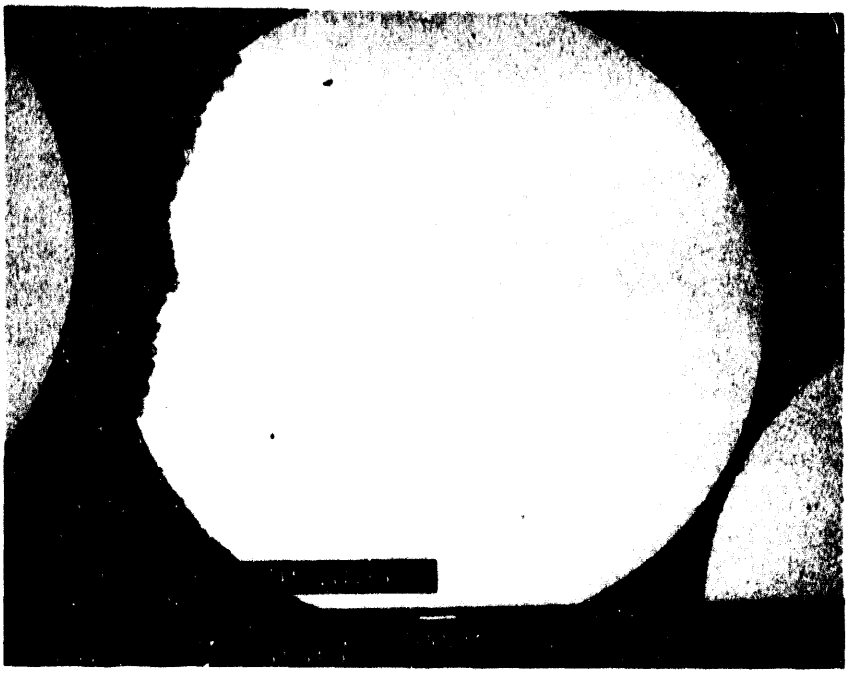

Figure 11. SEM photograph showing large deposit on one side of wire and bright areas on the surface of the wire.

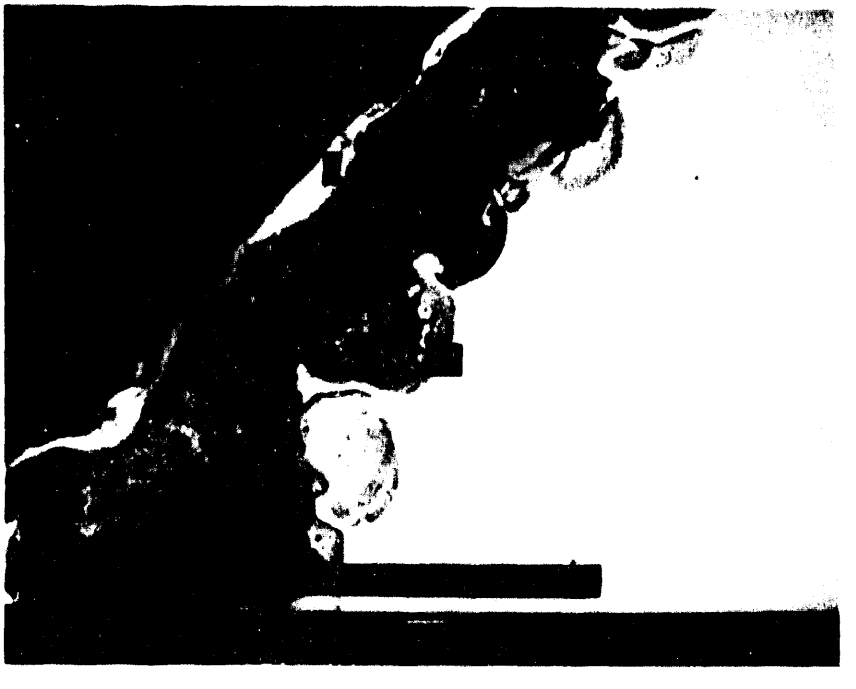

Figure 12. SEM photograph of the scale on the wire in Figure 11 at higher magnification, spectrum 8 is high in Ce and Pb, the nodule of spectrum 10 is high in Cl.

Cerium was used during these tests to simulate plutonium. Cerium is considered a reasonable surrogate for plutonium with the following qualifications:

- Cerium exhibits a similar chemistry in that much of its aqueous solution chemistry is similar to that of plutonium.
- Cerium exhibits a different oxidation state than plutonium so it is not directly analogous.
- Cerium potentially could form the strongly oxidizing ceric ion in the SCWO process and enhance the rapid corrosion of the reactor.
- Some of cerium's atomic characteristics do not perfectly match those of plutonium, however, they are closer than other available surrogates.

The metallurgical analysis of witness wires was one of the most interesting results of these tests. Several conclusions can be drawn from this analysis that are significant for evaluating the MODEC process, and for SCWO engineering in general. The most serious corrosion occurs in the preheat section and in the cooldown section, whereas in the reactor section where the temperature remains relatively constant and well above the critical temperature of water corrosion is mild or non-existent. It cannot be categorically concluded that the corrosion mechanisms in the preheat section are the same as those of the cooldown section, since much has happened to the fluid between these two points. The transition to and from the critical point, however, has an obvious influence on the severity of corrosion. The quantitative information presented in this report shows unacceptable levels of corrosion for the waste stream processed. This information should be moderated with the knowledge that the cerium used in the TRIM®SOL Surrogate may have greatly increased the level of corrosion. In processing TRIM®SOL without cerium, the level of corrosion should be less severe, although it is probable that the corrosion will still be too high. The corrosion results were probably skewed due to a pre-treatment process used on the system. The results would probably show less corrosion without this pre-treatment.

The MODEC SCWO process showed adequate operability for processing the TRIM®SOL Surrogate, although witness wire results showed some deposition. Of particular interest is the co-location of severe deposition with severe corrosion on the witness wires. Many deposits were deeply embedded in the base metal, while others appeared as build-up on the base metal. Local areas where metal loss was high were often filled in with salt deposits. The flow volume inside the reactor was maintained in the MODEC SCWO process, but the loss of metal and replacement with salt deposits in our data indicates this is only a stopgap measure. Other means of preventing or removing deposits during SCWO processing should be vigorously pursued.

SCWO holds promise in treating hazardous organic wastes. Controlled destruction efficiency can be obtained with existing SCWO technology. The key to continued progress of SCWO development is finding creative technological solutions for preventing corrosion and deposition when processing halogenated waste and waste with a large percentage of inorganics. Many paths exist for pursuing solutions, which leaves us optimistic about the future of SCWO.

ACKNOWLEDGMENTS - This work was prepared for the U.S. Department of Energy Office of Environmental Restoration and Waste Management under DOE Idaho Field Office contract no. DE-AC07-76ID01570. The authors wish to thank Brad Norby and Ron Mizia of Westinghouse Idaho Nuclear Corp., and Del Miley of EG&G Idaho for their contributions in the metallurgical analysis. The contributions of MODEC personnel were central to this work, including those of Michael Modell, Linda Lord, Evan Kuharich, Mike Rooney, Craig Ventola, and Dottie Rork. Other significant contributors include Kevin Liekhus, Chuck Mohr, Bill Bauer, Eric Peterson, and Glenn Thurston, all of EG&G Idaho.

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ULTRAVIOLET/HYDROGEN PEROXIDE PROCESS FOR TREATING AQUEOUS MIXED WASTE

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ABSTRACT. We have demonstrated that the ultraviolet light/ hydrogen peroxide (UV/H_2O_2) process is capable of completely destroying liquid organic wastes. Using the UV/H_2O_2 process, we destroyed two liquid wastes, ethylene glycol (water-soluble) and Trimsol (water-dispersible). For water-dispersible compounds, maintaining an emulsified condition is necessary for successful destruction of organics by the UV/H_2O_2 process. Conditions (e.g. pH, temperature, feeding rate of H_2O_2, etc.) for maximum efficiency of organic compound destruction have been identified during careful, parametric investigations.

INTRODUCTION

The UV light-catalyzed oxidation of organics by H_2O_2 (UV/H_2O_2 process) is one of the advanced oxidation processes(1) that has been used to treat large volumes of effluent-containing dilute organic contaminants. With appropriate UV wavelengths (200–250 nm), UV/H_2O_2 undergoes photochemical decomposition to produce $OH^{\cdot}$ radicals (2,3) that are strong oxidants, capable of oxidizing most organic compounds stepwise to complete mineralization (i.e., all carbon atoms are oxidized to CO_2, all hydrogen atoms to H_2O and other nonmetallic elements to corresponding anions). When used for applications such as groundwater remediation, UV photolysis is successful if all the toxic organic compounds are converted to nontoxic compounds. However, to successfully convert mixed waste containing hazardous organics to low-level radioactive waste, the UV photolysis process would need to completely destroy all the organic compounds in the mixed-waste stream. The process has not yet been demonstrated for treating this class of mixed wastes.

In this report, we document our progress on demonstrating the destruction/treatment of two liquid organic compounds. They are ethylene glycol (a model compound for water-soluble nonhalogenated organics) and Trimsol oil, a commercial mixture of organic compounds, which is a water-dispersible lubricant used in metal cutting.

EXPERIMENTAL WORK

Apparatus

We obtained a functional UV/H_2O_2 system from Peroxidation System, Inc. (Phoenix, Arizona) and modified the system as follows:

- A gas-collecting system was added to allow quantitative measurement of gases evolved under constant pressure.
- A residual gas analyzer (RGA) was installed on the gas collecting system to determine the

unwanted by-products produced.

- An optical probe, connected to a UV-visible spectrometer by an optical fiber, was also installed in the reactor chamber to measure the spectral distribution and the attenuation of UV light in the process stream.

The lamp is a medium high-pressure mercury lamp (25-cm long with an internal diameter of 1.6 cm) with an output power of ~2 kW. A peristaltic pump adds H_2O_2 solution to the system and continuously circulates the solution during the process. Figure 1 shows a diagram of the completed system. This instrumentation has given us unusual insight into the process.

Experimental Results and Discussion on Ethylene Glycol (EG), a Model Compound for Water-Soluble Nonhalogenated Organics

Mixtures of approximately 0.5% EG in water were poured into the reaction chamber. The rate of H_2O_2 solution addition was ~1.0 mL/min. The results of three runs (Fig 2) clearly show that the total organic carbon (TOC) can be reduced to near-zero concentration and demonstrate that this type of organic compound can be treated/destroyed by the process. However, these results were not obtained under the most efficient process conditions. We believe that feeding the EG with a peristaltic pump will allow the process to operate at lower EG concentrations, thereby enhancing process efficiency. EG absorbs light near 200 nm and competes with H_2O_2 for available UV light. Furthermore, higher concentrations of EG tends to produce undesirably higher concentrations of intermediates (methanol, ethanol, etc. detected and measured by mass spectrometry). These intermediates are quite volatile and can escape from the process solution as gaseous by-products. In a circulated and sealed system, all intermediates will eventually be destroyed.

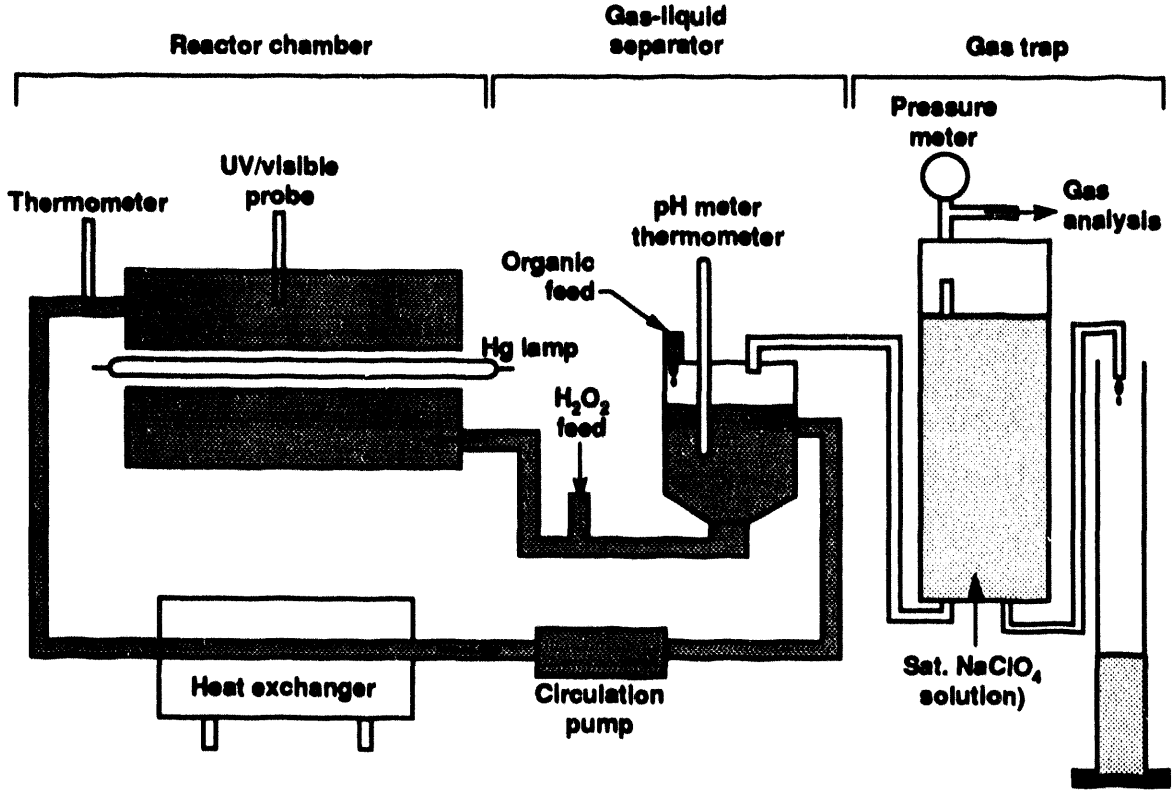

Figure 1. UV/H_2O_2 reactor(LLNL).

During the photolysis of EG solutions with no addition of H_2O_2, the pH dropped from 7.5 to 3.4. With the addition of 30% or 10% H_2O_2 solutions, the pH dropped to 2.5. This drop in pH is probably due to the formation of intermediates, such as formic acid and acetic acid, which are found in the mediated electrochemical oxidation of EG by Ag(II) in nitric acid solutions(4). A blank run was also conducted to generate baseline data. A mixture of 5 mL of 1% EG solution and 5 mL of 10% H_2O_2 was mixed together for 3 h without UV light. In this case, no reaction was observed between EG and H_2O_2.

Experiments on Timsol, a Model Compound for Water-Dispersible Organic Mixtures

Composition of Trimsol. Trimsol is a mixture of organic compounds: 30–40% petroleum oil, 20–30% petroleum sulfonate, 20–30% chlorinated alkene polymer, 1–10% nonionic surfactant, aromatic alcohol, propylene glycol ether, <1% blue-green dye, silicone defoamer, and substituted indole. The remainder is water. This composition is provided by the manufacturer. The overall elemental analysis is C, 68.54%; H, 10.44%; Cl, 11.1%; O, 7.48%; S, 1.0% and N, 0.06%. The density of Trimsol is approximately 1 g/mL.

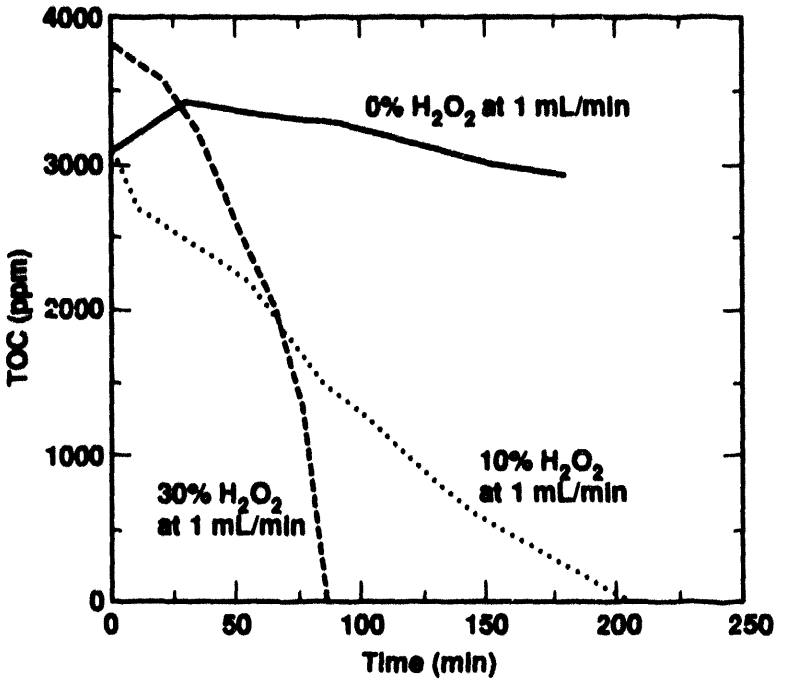

Figure 2. TOC vs Time for EG destruction with various H2O2 concentrations.

The First Experiment. The first experiment with Trimsol was carried out with an initial Trimsol to water ratio of 1:250 and a pH of 8.3. A solution of 30% H_2O_2 was added at a rate of 2 mL/min. Twenty minutes after starting the experiment, the pH of the mixture dropped to 2.2, probably due to the formation of HCl. We have found that the dispersability of Trimsol and water diminishes in acidic solutions. With the immiscible components of Trimsol separated from water, the UV/H_2O_2 treatment process produces globs of grease as a by-product. Two ways to avoid this problem are (1) to control the pH of the solution or (2) find other means to maintain emulsification of the water-Trimsol mixture. We decided to control the pH with a borate buffer solution made from boric acid and sodium borate (pH 9-10) because borates have very low optical absorption between 190 and 250 nm, which is the most effective region of the UV spectrum for dissociating H_2O_2 into OH radicals.

Experimental Conditions for Subsequent Runs. We found that some compounds of Trimsol dissolve in water and absorb light between 200 and 250 nm. In subsequent runs, Trimsol was added to the system by a peristaltic pump to maintain a constant low concentration of unreacted Trimsol. Several experiments were carried out under the following conditions: fixed feed rate of solution (2.2 mL/min) with various concentrations of H_2O_2; fixed feed rate of Trimsol (2.0 mL/h); fixed temperature (40 ± 2 °C); fixed starting process volume (2.5 L) buffered at pH~9 (established by ~0.1 *M* borate solution); and a fixed circulation rate (5.7 L/min). In this series of runs, the gas collection system was not used. The pH of the reaction volume never dropped below 7, and no separation of phases was observed.

RESULTS AND DISCUSSION

Effects of Photolysis on Trimsol Destruction

When Trimsol was the only species fed into the system and the lamp was switched off, the rate of TOC increase was 5.8 ppm/min in a period of ~2 h. Because the increase of TOC is linearly proportional to time, we concluded that the Trimsol was uniformly dispersed throughout the solution. The same rate of TOC increase was observed with the Hg lamp on and no H_2O_2 present. Thus, direct photolysis makes only a minor contribution to the destruction of this mixture of organic compounds.

Feeding Rate of H_2O_2

When H_2O_2 is fed, OH radicals form and can attack organic compounds or they can attack H_2O_2 to produce O_2. To minimize excess H_2O_2 parasitic consumption of OH radicals, it is essential to find the optimum feed rate of H_2O_2 for a fixed feed rate of Trimsol. To maintain the same total volume in the reactor, the H_2O_2 feed rate was changed by using a constant pumping rate while feeding solutions with different concentrations of H_2O_2.

In each run, samples were taken from the process at 20 min intervals for TOC analysis. Figure 3 is a plot of TOC against time that shows that the rate of TOC increase does not change during the first two hours, even as the concentration of fed H_2O_2 increases from 5 to 30 wt%. After turning off the Trimsol but continuing UV irradiation, a faster decrease in TOC level was observed as the concentrations of fed H_2O_2 increased from 7.5 to 30 wt%. We need to conduct experiments at the same conditions but with extended duration; we recommend durations between 15 and 30 hr. From the plots of TOC against time that show steady-state TOC levels, we can determine the most efficient H_2O_2feed rate. For example, a lower steady-state TOC indicates a faster rate of Trimsol destruction/conversion. Based upon these experimental data, we have decided to use 30 wt% H_2O_2 in future runs.

Achieving Steady-State Destruction of Trimsol

We have demonstrated the feasibility of destroying Trimsol by continuously feeding Trimsol to the UV/H_2O_2 process while maintaining a constant (time-invariant) TOC concentration. A steady-state destruction rate of Trimsol can be deduced from our results. Under these conditions, the rate of destruction is identical to the feed rate. Figure 4 shows the results for a 15-h experiment. The TOC level reached a steady of ~400 ppm after 5 h of photolysis. Therefore the rate of Trimsol destruction is 2.0 mL/min.

After the 15-h run, we conducted two experiments of longer duration. The first, lasting 60 h, was intended to study the effect of HCl formation and its interaction with the chemical buffer. Based on the results of TOC analyses and visual observations, we concluded that phase separation commences slowly only after the pH falls below 7.5. Future process designs must consider phase separation problems caused by the formation of HCl (acidification).

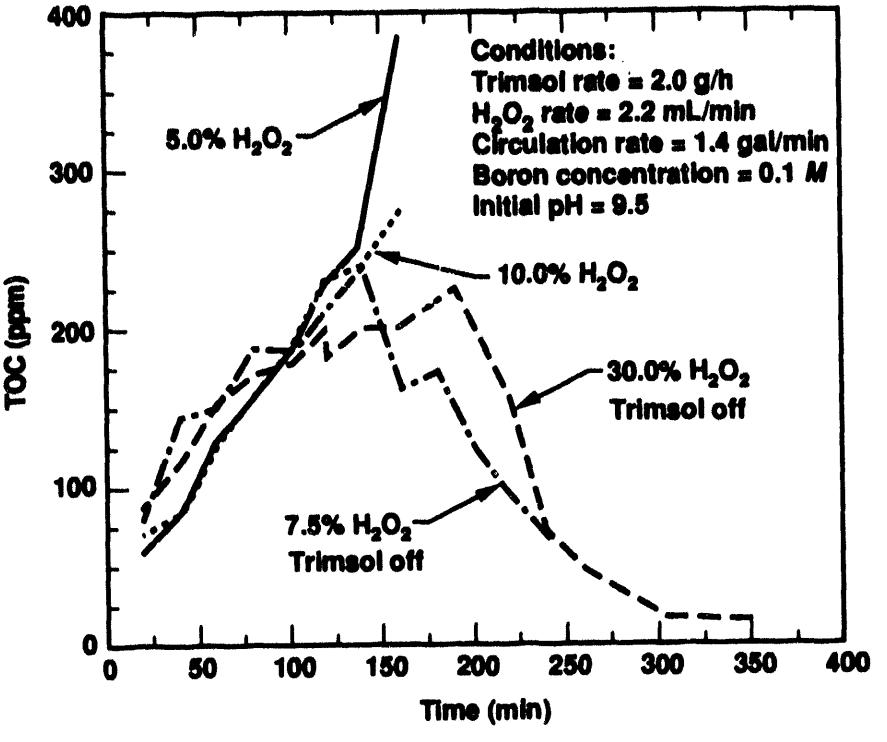

Figure 3. TOC vs Time for Timosol destruction with various H_2O_2 concentrations.

The second long experiment, lasting 78 h, was conducted with the same conditions as the 60-h experiment except that the pH was maintained higher than 7.5 by continually adding buffer solution. The purpose of this experiment was to see if Trimsol-water emulsions can be maintained during the destruction process, and if a steady-state TOC concentration can be maintained for periods longer than 10 h.

Figure 5 shows the results of this experiment. The TOC level seemed to reach steady-state at a TOC concentration of 850 ppm after 15 h , and then slowly increase to 1300 ppm during the next 40 h. Figure 5 shows that it took longer (~15 h) for the TOC concentration to reach a constant level (850 ppm), which was higher than that shown in Figure 4. Subsequently, the TOC concentration increased from 850 to 1300 ppm. We believe this is a result of (1) an increase in the rate of Trimsol addition due to the stretched tubing used in peristaltic pump ; and (2) the build-up of a concentration of bicarbonate ions (formed from CO_2). Note that the bicarbonate ion has a molar extinction coefficient of ~100 at 200 nm and a pH of 9.9 (5) and it is a scavenger of $OH^{\cdot}$(6). The effect of bicarbonate on the steady-state TOC concentration will be examined in the future.

Effects of Temperature

Preliminary studies of the effect of temperature on Trimsol destruction have been performed, but no conclusive results are yet available. The circulation pump could not handle the amount of gases produced at higher temperatures. It will be replaced in the future runs.

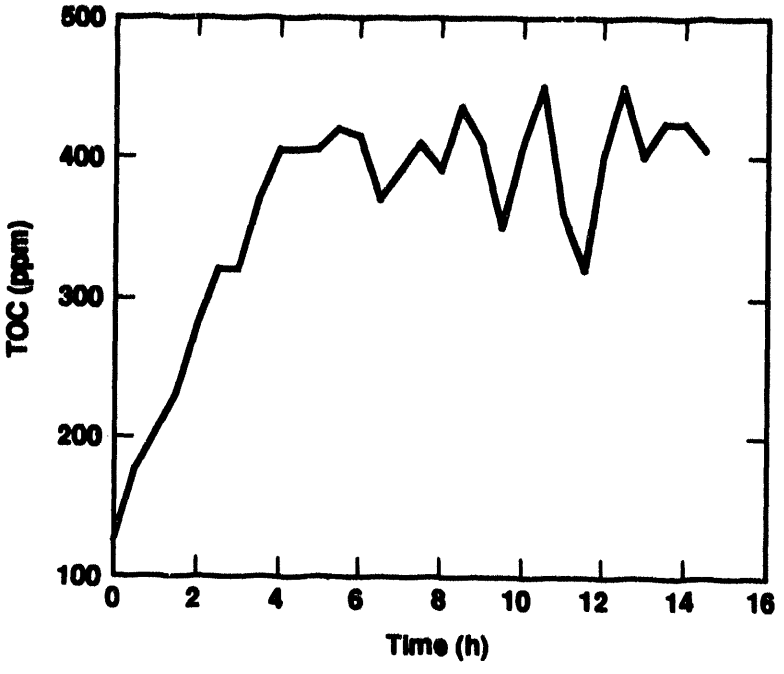

Figure 4. Timosol destruction during 15 h run reached a steady state of ~400 ppm C.

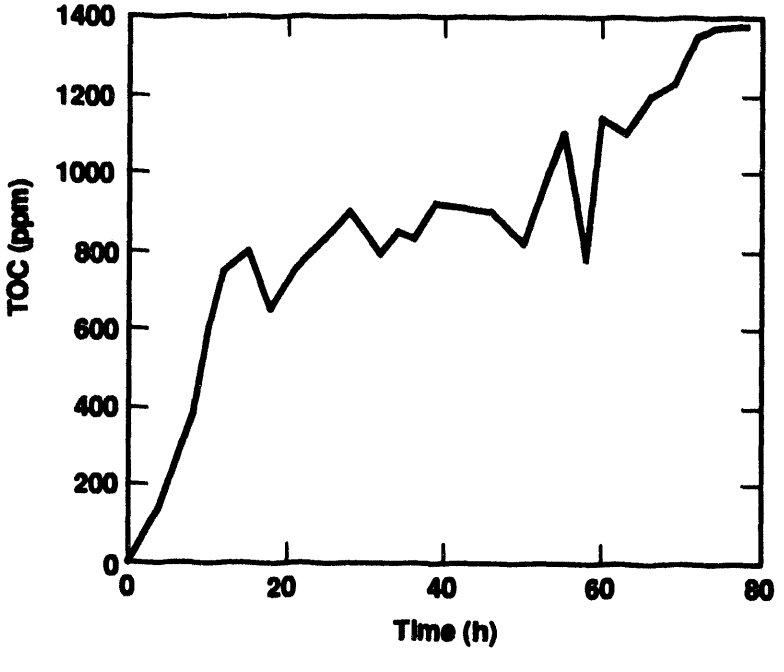

Figure 5. Timosol destruction during 78 h run.

Gas-Collection System

In conducting carbon balances during Trimsol-destruction experiments, the gas-collection system for O_2 and CO_2 consisted of a manometer filled with solution of saturated sodium perchlorate (~5*M*) and perchloric acid (10 mL of concentrated acid). The volume was 4 L and the pH was ~1. Carbon dioxide is not expected to dissolve in the solution. The maximum amount of gas that can be collected by the manometer is about 3.5 L at 1 atm and 25°C. The experimental plan for performing carbon balance was to use TOC and total inorganic carbon (TIC) (i.e., bicarbonate and carbonate from CO_2) analyses of solutions before and after photolysis, and samples of product gas (primarily CO_2).

wo experiments were done with 1.75 g and 1.22 g of Trimsol, respectively. Trimsol and 2.5 L of buffer solution were added to the reactor and circulated. After the circulation was stopped, the whole system was at room temperature and was opened to the atmosphere. The gas-collection system was then closed off from the atmosphere and the Trimsol destruction reaction was started. Excess H_2O_2 in solution produces only O_2. Because the volume of the gas-collection system is limited, the addition of H_2O_2 to the reactor was controlled by turning the peristaltic pump on and off to minimize total O_2 production. We assumed that destruction was completed when the mixture became clear and the molar H_2O_2 feed rate was identical to the molar production rate of gas in the gas-collection system. We collected a liquid sample for TOC and TIC analyses and cooled the system to room temperature. After stopping circulation within the process, the pressure inside the manometer was allowed to equilibrate with the ambient environment. The total volume of product gas was recorded and gas samples were taken for mass spectrometric analyses. Table 1 summarizes the results.

Table 1. Carbon balance for two destruction runs on Trimsol.

Timosol (g)	TOC Calculate[a] (millimole C)	TIC after run (millimole C)	TOC after run (millimole C)	CO_2 (millimole C)	Coabon balance (%)
1.75	100	85	9	0.1	94.1
1.22	69.7	66.1	3	0.1	99.3

[a]TOC calculate is the total number of millimoles of carbon added to the reactor. The C content of Trimsol is 68.54%.

Although research and development on the UV/H_2O_2 process applied to Trimsol is not yet complete, the process seems not cost-effective for destroying dewatered or neat Trimsol. Generally, real Trimsol wastes contain 2-5 wt% of Trimsol and 95-98% water. No attempt should be made to dewater such wastes. Instead, Trimsol should be treated with small quantity of HCl acid to drop the pH of mixture to ~3 which causes a separation of phases. Subsequently, only the aqueous phase would be treated by the UV/H_2O_2 process.

FUTURE PLANS

Successful implementation of UV/H_2O_2 as a process for treating aqueous mixed waste streams depends on maximizing the overall efficiency of the process. The lamp (light source) is a critical part of this

technology. Although mercury lamps are the most commonly used in UV/H_2O_2 processes, they are probably not the most efficient source for treating aqueous mixed wastes. We will investigate a xenon flash lamp-based treatment system developed by Purus, Inc. and plan to conduct a direct comparison between the two lamps.

SUMMARY

The UV/H_2O_2 process may be an important alternative technology for the treatment of aqueous mixed-waste streams. Among its many advantages are: 1) the process is conducted at ambient conditions and easily controlled, 2) only benign chemicals are added and none are solid-waste forming additives, 3) removal of by-products from the system is easy-CO_2, H_2O and mineral acids, 4) it has the potential for treating moderate concentrations (a few percent) of organic compounds, and 5) the technology should easily satisfy most regulatory requirement.

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ADVANCED OXIDATION AND REDUCTION PROCESSES: CLOSED-LOOP APPLICATIONS FOR MIXED WASTE

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ABSTRACT. At Los Alamos we are engaged in applying innovative oxidation and reduction technologies to the destruction of hazardous organics. Nonthermal plasmas and relativistic electron-beams both involve the generation of free radicals and are applicable to a wide variety of mixed waste as closed-loop designs can be easily engineered. Silent discharge plasmas (SDP), long used for the generation of ozone, have been demonstrated in the laboratory to be effective in destroying hazardous organic compounds and offer an alternative to existing post-incineration and off-gas treatments. SDP generates very energetic electrons which efficiently create reactive free radicals, without adding the enthalpy associated with very high gas temperatures. A SDP cell has been used as a second stage to a LANL designed, packed-bed reactor (PBR) and has demonstrated Destruction and Removal Efficiencies (DREs) as high as 99.9999% for a variety of combustible liquid and gas-based waste streams containing scintillation fluids, nitrates, polychlorinated biphenyls (PCB) surrogates, and both chlorinated and fluorinated solvents. Radiolytic treatment of waste using electron-beams and/or bremsstrahlung can be applied to a wide range of waste media (liquids, sludges, and solids). The efficacy and economy of these systems has been demonstrated for aqueous waste through both laboratory and pilot scale studies. We will present recent experimental and theoretical results for systems using stand alone SDP, combined PBR/SDP, and electron-beam treatment methods.

INTRODUCTION

Historically, combustible wastes (including those with radioactive metal contamination) within the U.S. Department of Energy (DOE) and U.S. Department of Defense (DOD) complexes have been incinerated to reduce volumes and, in the case of hazardous mixed wastes contaminated with organics, to destroy the hazardous organic constituents. Growing legislative and social concerns are leading to an increased demand for a reduction in the amount of wastes released to the environment through flue gas stacks, liquid waste streams, and other sources. U.S. Environmental Protection Agency (EPA) and Resource Conservation and Recovery Act (RCRA) regulations on the release of hazardous compounds to the environment will become increasingly stringent in the next decade. Although the EPA still considers incineration the best demonstrated available technology for many combustible wastes, public acceptance of incineration has declined to a point where alternatives must be evaluated. Similarly, licensing of an incinerator in today's climate may take seven or more years. Combining the incineration problem of hazardous organics with the potential for the release of radioactive materials in mixed waste treatment has virtually rendered conventional incineration as a totally unacceptable solution. Thus the DOE and DOD complexes must proceed to develop environmentally acceptable mixed waste treatment technologies, particularly those which minimize (or eliminate) uncontrolled emissions.

The conventional approach to organic destruction is through combustion of the material. Although this can usually be a one-step process, difficult, noncombustible materials such as polychlorinated biphenyls (PCBs) require a two-stage process, with the second stage running at a very high temperature. In all cases, the

chemistry is dependent on the generation and propagation of free radicals such as $O(^3P)$, OH, and H. The efficiency of production for these free radicals depends primarily on the temperature of the combustion. For waste materials that do not contain highly combustible organic materials, fuel (such as hydrogen, methane, and methanol) that can generate the high temperatures required must be added to render the mixture highly combustible. This increases the effluent volume and, if emission based taxes are implemented, system cost.

The Silent Discharge Plasma

The use of plasmas can provide an efficient way to produce the free radical concentrations required for complete destruction of waste (1). Plasmas can generate very energetic ("hot") electrons (typical energy range of 1-10 eV), which are very efficient at creating free radicals without adding the enthalpy associated with very high gas temperatures. Thus, reaction rates associated with temperatures of 10,000 K to 100,000 K can be realized while the actual gas temperatures remain near ambient. These typical "cold plasmas" can be very energy efficient for waste destruction because most of the work goes into enhancing the chemistry without significantly raising the gas temperature and without adding additional fuel to the process. Compounds destroyed by these methods include: SO_x, NO_x, trichloroethylene (TCE), perchloroethylene (PCE), TCA, CCl_4, xylene, toluene, p-cumene and PCB surrogates. One of these "cold plasma" processes, the silent discharge plasma or SDP, offers superior treatment capabilities compared to other cold plasma techniques (corona for example). SDP is such a mature, reliable, and economical process that ozonation is the method of choice for sanitary water treatment in Europe and some parts of the US.

Such silent discharge cold plasmas are commonly produced with near-atmospheric pressure discharges called dielectric barrier or silent discharges (2). Typically, one or both electrodes are covered with dielectric layers (e.g., glass), which separate them from the gas (Fig. 1). The geometry can be either planar or cylindrical; in the latter, concentric tubes rather than flat plates are used. This arrangement is an old one, first employed by Siemens in 1857. At gas pressures of 1-10 atm and gap spacings of a few mm, without the dielectric a few localized intense arcs would develop in the gas between the metal electrodes. With a dielectric and the application of alternating high voltages (50- or 60-Hz power frequency to several kHz), substantial quantities of plasma are created by a large number of "microdischarges" in the gas, which are statistically spread in space and time, filling the reactor volume.

Because of the short duration (a few ns) of the microdischarges and the low ion mobilities, electrical energy in silent discharges is principally coupled into electron channels – electrons, ions, and gas do not equilibrate – so the electrons are "hot", while the other species are "cold." This results in a very efficient transfer of electrical energy to electronic excitations of molecules and/or chemical processes in the plasma, while the temperature of the bulk medium remains at ambient temperature. The ability to maintain a discharge does not depend highly on the composition of the feed gas (nebulized organic or aqueous/organic mixtures) and requires no added fuel. Since most of the electrical energy goes into free radical formation and very little into heating the gas the process has demonstrated very high destruction efficiencies yielding very attractive economics of kilograms of waste destroyed per kW-hr of electricity consumed. Secondary waste streams typically contain the completely oxidized products of the feed constituents, primarily CO_2 and H_2O, with HCl from chlorocarbon waste.

The Packed-Bed Reactor

We are also developing packed-bed reactor (PBR) technology (3) as an alternative to incineration for hazardous organic liquid wastes. The primary motivation for our current effort is the need to develop innovative treatment technologies to process the large volumes of chlorocarbon contaminated machining oils and aqueous emulsions presently stored at the Rocky Flats Plant. These machining liquids, generated during the preparations of nuclear weapon materials, are contaminated with low levels of plutonium. Other waste

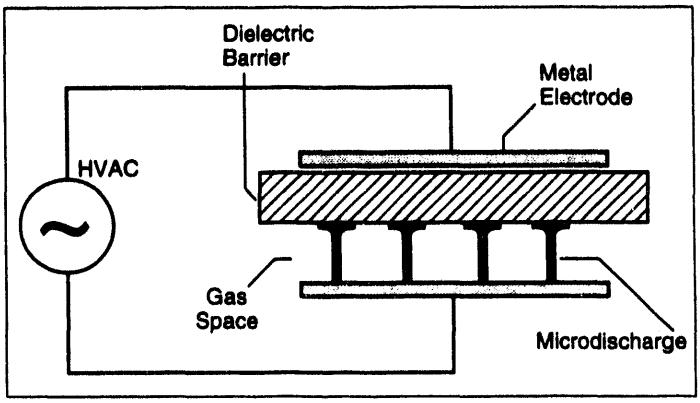

Figure 1. Schematic showing the flat dielectric barrier configuration used to producesilent discharge plasma microdischarges.

streams targeted by this technology include machining fluids contaminated with PCBs and low levels of tritium. Results have been obtained using prepared mixtures of machining oil and TCE, TCA, Freon TF, and CCl_4 with flow rates of up to 215 L/min of oxidizing gas and 6 g/min of liquid mixtures.

Thermal PBR technology has several distinct advantages for the treatment of combustible liquid wastes: First, the PBR operates below normal flammability limits and relies upon an external energy source to initiate and control the chemical reactions. Second, the heat of reaction can be used to sustain the operation of the PBR once the organic flow begins; hence, reducing or eliminating further electrical input. Third, because the technology is relatively simple, the overall initial and operating cost should be modest. Fourth, since the technology is rugged, the scalability, survivability, and maintainability of a PBR system should be extremely high.

A diagram of the treatment system with the PBR as the first stage is shown in Fig. 2. The PBR consists of the following major parts: main reactor enclosure (cylindrical metal pipe), bed packing material (alumina pellets), and an electric furnace. As currently designed, the bed reactor is a tube with an outer diameter of 16.4 cm and a length of 105 to 120 cm. The liquid is atomized above the bed using a simple axisymmetric, oxidizer-gas-assisted nozzle. The liquid gasifies with passage through the bed and reacts with the oxidant and products of thermal decomposition producing easily handled materials (primarily CO_2, H_2O, and HCl) before reaching the bed exit. After exiting the bed, the gas is cooled down by passing through a heat exchanger, analyzed to determine its composition, and sent through additional stages and treatment processes as necessary. Historically, for applications like stack gas purification or catalytic enhanced processes, PBR systems have used a large variety of bed materials and hence, reaction mechanisms. For our current process, alumina appears to be a good bed material. Other materials such as calcium carbonate could be added to enhance the removal of certain compounds such as HCl. The initial heat source for the reactor is an external electric tube furnace. An operating temperature between 500 and 1300°C is generally required depending on the fluid being treated. While the current furnace limits the bed reactor to a maximum diameter of about 16.5 cm, tube furnaces are commercially available up to about 100 cm in diameter.

The current data is primarily from the 6.4-cm OD reactor. Initial testing of a 15-cm ID PBR has recently been completed. This system will allow studies of gas and liquid chemical conversion processes at gas flow rates up to a range of 300 to 700 slm and organic liquid injection rates up to about 100 g/min (about 6 kg/hr), depending on the water/organic ratio. Based on current data from the 6.4-cm OD reactor, a system designed for operation at a liquid injection rate of 1 kg/min would have an OD of about 30 to 45 cm with a bed length of about 1 m.

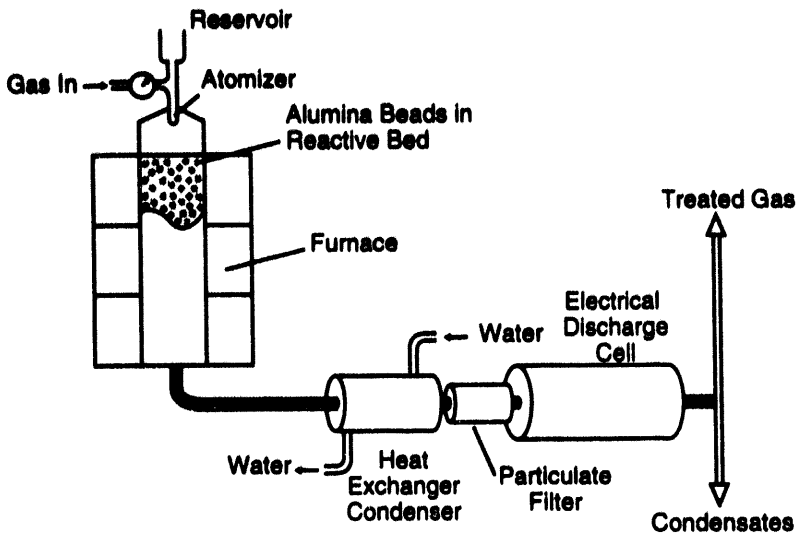

Figure 2. Schematic of combined SDP/packed-bed reactor waste processor used in this work for combustion of scintillation fluids and machining oils with entrained hazardous components.

Electron-Beam Treatment

High-energy electron beams and x rays (bremsstrahlung) belong to a class of technologies generally referred to as radiolytic methods. These methods have been demonstrated, both in the laboratory and in pilot plants, to effectively destroy hazardous organic wastes, particularly chlorinated hydrocarbons (4). We have established collaborations with industry, academia and other national laboratories to promote radiolytic (electron-beam) waste treatment technology. The hazardous components of particular concern in mixed wastes are those on the EPA Superfund list of toxic organics and other fluids which are typically found in process streams, stored materials, and ground water. Within DOE, EM-30 and EM-40 need aqueous and mixed waste technologies that address the following key points:

- Process must handle a broad spectrum of hazardous wastes as present aqueous treatment technologies do not do not handle higher solids content or sludges, and are too compound-selective; therefore, cost of present technologies too sensitive to waste type.
- Process should provide high throughput and short residence times.
- Standoff capability (major part of equipment not in contact with radioactive components) desired for mixed wastes.
- Process should provide broad dynamic range of treatment capability.

Existing technologies fail to provide effective and economical means of addressing these problems. Radiolytic treatment technology shows promise for addressing these needs as well as contributing solutions to mixed radiochemical waste treatment problems of key importance to the DOE Complex.

Radiolytic treatment has advantages over existing industrial waste treatment technologies because it is not sensitive to the treatability of the contaminant or the particular target species; it treats waste streams of varied composition (including solids characteristic of mixed wastes), has a short residence treatment time, and is a superior de-halogenator. As evidenced by earlier studies, radiolytic treatment technology has an established engineering base, is presently economically competitive with other methods [Fig. 3 (5)] and is envisioned to be less expensive when new accelerator technology is implemented. Hanford, for example,

has identified the need for removal/destruction of organic compounds, nitrates, and ferrocyanides from single-shell tank wastes. Radiolytic processes show promise for the removal of these wastes, and the treatment of sludges as well, because of the presence of both oxidative and reductive free radicals.

EXPERIMENTAL RESULTS

SDP Treatment of Off-Gases

The prototype SDP laboratory at Los Alamos uses a planar cell to treat waste streams at up to 10 L/min. The cell has approximate dimensions of 71 cm long, 18 cm wide and 2.5 mm gap, giving a mean discharge area of 1236 cm^2, and an active volume of 310 cm^3. A cylindrical cell designed for operation at higher temperatures can be inserted in a surrounding furnace. Higher temperature operation is desired because reaction rate coefficients involving OH increase with temperature. This cell has an active volume of 215 cm^3. The planar cell was used for the data reported here. Our main electrical power supply is a series inverter which switches charged capacitors through a high-quality pulse transformer by high-power thyristors. This unit supplies up to 4 kW of power at repetition rates to 3 kHz. Other driving circuits include commercial systems built for ozonation, fast pulse forming networks and simple audiofrequency amplifiers.

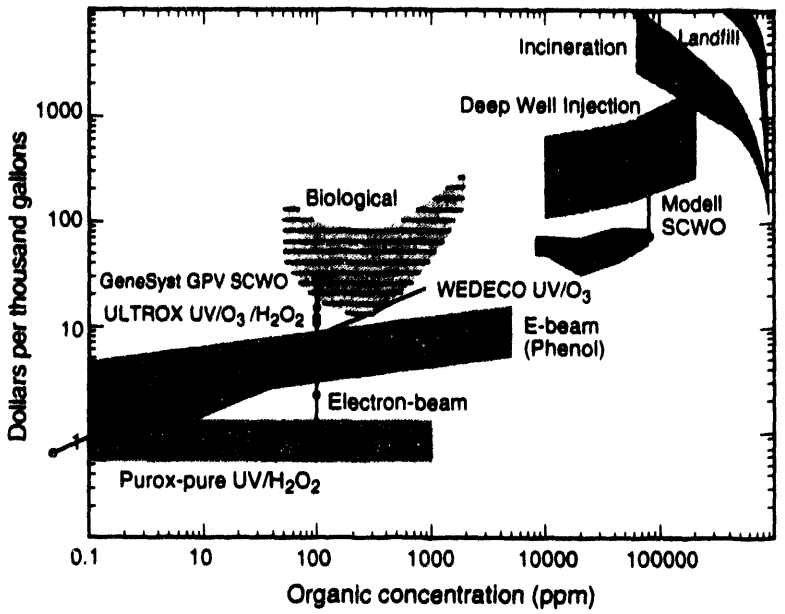

Figure 3. Cost diagram of various waste water treatment methods.

In order to determine the destruction efficiency of any process, two measurements must be made. The first is the power supplied to the system. The usual method of deriving electrical power, $\langle W \rangle = V^*I$ is difficult to implement for SDP due the transient nature of the current. A formula, using easily measured parameters, for the average power dissipated within a silent discharge has been developed by Manley (6):

$$\langle W \rangle = 4 f V_i C_d \{V_o - [(C_d+C_g) / C_d] V_i\} . \quad (1)$$

Where f is the frequency of the applied voltage in Hz, C_d and C_g are the dielectric and gas capacitances, respectively, in Farads, and V_i and V_o are the gas ignition and peak applied voltages, respectively, in Volts.

Both V_i and V_o are taken from a measurement of the total voltage appearing across the cell, V_{cell}. This equation has proven to be useful for a wide range of applied voltage waveforms. An alternative method uses a simple integrating circuit to measure the transported charge, Q. At an applied voltage, the gas does not breakdown and Q is proportional to and in phase with V_{cell}. Above breakdown, losses within the gas discharge phase shift Q and the Q-V plot generates a figure whose area corresponds to the power dissipated in the gas per cycle. Calculations using equation 1 and the area of the Q-V plot agree to 5%, well within the error of the original measurements.

The effluent from the SDP reactor is distributed to a gas manifold for the second measurement: chemical analysis. Analytical capabilities include infrared (IR) spectrometry, mass spectrometry (MS), and gas chromatography. The IR and MS systems are used primarily to search for, and identify, intermediate compounds produced in the discharge. The gas chromatograph (GC) monitors the concentration of the specific contaminant under study.

To determine optimal treatment conditions we have conducted power scaling experiments with TCE and CCl_4. Figure 4 shows a representative plot of measured destruction rates for the listed gas flow and composition. The TCE and CCl_4 are diluted into a 78/19/3 mix of argon/oxygen/H_2O. Other compounds destroyed using SDP include: hydrocarbons, CFCs, toluene, xylene, p-cumene, dichlorobenzene, NO_x and SO_x. System optimization continues.

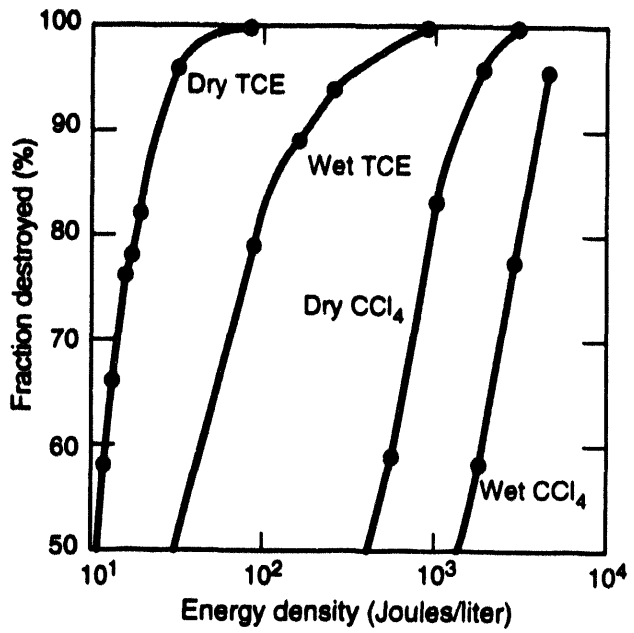

Figure 4. Summary of experimental data showing destruction of TCE and CCl_4 by the LANL SDP cell.

In order to compare varied experimental conditions, a figure of merit, can be determined by the energy delivered to the plasma per hazardous molecule removed from the gas stream. The average power, <W>, is divided by the flow rate, Q, and hazardous compound concentration, C. Using convenient units, this can be expressed as kW-hr/kg – or the number of kilowatt-hours needed to remove one kilogram of hazardous

compound. For the data in Fig. 4, we calculate a figure of merit of 84 kW-hr/kg for >>99% removal of TCE, and 270 kW-hr/kg for >90% removal of CCl_4. These results are consistent with the modeling efforts underway at LANL and our coworkers at the U. of Illinois and Auburn (7).

Combined PBR/SDP Treatment of Liquids

The SDP and PBR sub-systems have been integrated to treat contaminated cutting oils. The PBR gaseous effluent was sent directly to the SDP reactor (after condensing most of the liquid) for further treatment. Chlorocarbons in the final effluent were well below 100 ppb. Results (using an infrared spectrophotometer, a gas chromatograph (GC), and a mass spectrometer for diagnostics) indicate that chlorocarbon compounds such as TCE and CCl_4 can be removed by the PBR to 0.1 ppm levels during steady state operation. During start up, transient behavior in the PBR does allow larger concentrations of chlorocarbons and reaction products to remain in the effluent stream. During this startup period, the power applied to the SDP stage would be increased to reduce the effluent concentrations to acceptable levels. Figure 5 shows a time history of the effluent during a TCE test measured with the GC.

A series of test runs have determined the effectiveness of PBR/SDP treatment of 1,2-dichlorobenzene (DCB). The system successfully reduced DCB levels to below 1 ppm. The EPA suggests DCB as a surrogate for PCBs, which are controlled by Toxic Substance Controll Act (TSCA). The index of incinerability for DCB is 24, compared to 30 for PCB. The lower the number, the more difficult to incinerate. Tests were conducted for both pure samples and samples mixed with 80% oil. During startup data show DCB levels around 3 ppm. This is reduced to around 2 ppm as the CO concentration decreases. It appears that the addition of oil assists the combustion of the DCB. Treatment of the PBR off-gases by the SDP substantially reduce DCB levels. At a delivered energy density of 2.6 kJ/L DCB levels are below 500 ppb. For a delivered fraction of 20% DCB this corresponds to better than 0.999997 destruction – for an unoptimized system. As the run progressed, the flow rate was increased to 1.0 mL/min. The CO level continued to fall as did the DCB level from the packed-bed. Thermocouple data suggest a longer, higher temperature zone within the bed, which increases the residence time of the DCB in the reaction zone. Additional studies will optimize the temperature profile in the packed bed.

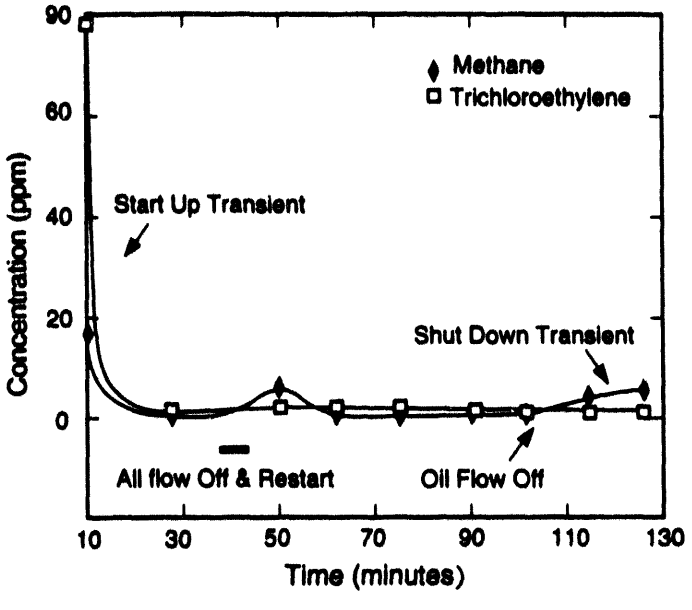

Figure 5. Effluent concentration as a function of PBR running time. Influent: 3% TCE in machining oil.

To assess the feasibility of destroying nitrates with the PBR/SDP system we processed a 3M solution of $NaNO_3$ in water through our small PBR, with and without a reducing gas, and analyzed the effluent with a FTIR spectrometer. The preliminary results are encouraging. Figure 6 represents a composite of three separate figures showing FTIR traces of the PBR effluent with different influent compositions. Panel (a) shows an FTIR baseline trace of the PBR effluent with argon only. The CO_2, water, etc., peaks are due to residual reactions and contamination from PBR processing of oils. The trace shown in Panel (b) displays the apparent generation of NO_x products with a feed of argon + the 3M $NaNO_3$ solution, presumably produced through thermal cracking of the $NaNO_3$. Panel (c) shows an effluent trace after introduction of a (4.8%)H_2/argon mixture into the PBR with the $NaNO_3$ solution. The NO_x peaks are no longer visible. Although further testing and full diagnostic implementation is required for complete verification and assessment system performance and products, these initial runs indicate that the nitrate concentration is reduced by processing through a heated PBR (~900°C) operating with a hydrogen-containing atmosphere. The second stage SDP reactor will remove any NO_x from the exhaust.

The design of a pilot plant is influenced by waste type and treatment throughput. Based on the results discussed above, it is reasonable to conclude that an oil/solvent processing pilot, based on a closed-loop PBR/SDP design, is straightforward in concept. In conjunction with our work for Rocky Flats, we have explored specific "modular" plant designs. For example, a system operating in the range of 3-10 kg/hr would use three or four 15-cm PBRs and two stacks of SDP cells operating in parallel (Fig. 7). The system is low cost, simple to construct and easy to maintain. The system proposed (8) is shown in Fig. 8.

Electron-Beam Treatment

We have configured an existing electron accelerator for technology evaluation studies and demonstrated the destruction of two hazardous organic compounds characteristic of priority mixed wastes. The test bed operates in single-pulse mode (65-ns pulse width), typically producing beam voltages of 1.5-2.0 MeV and

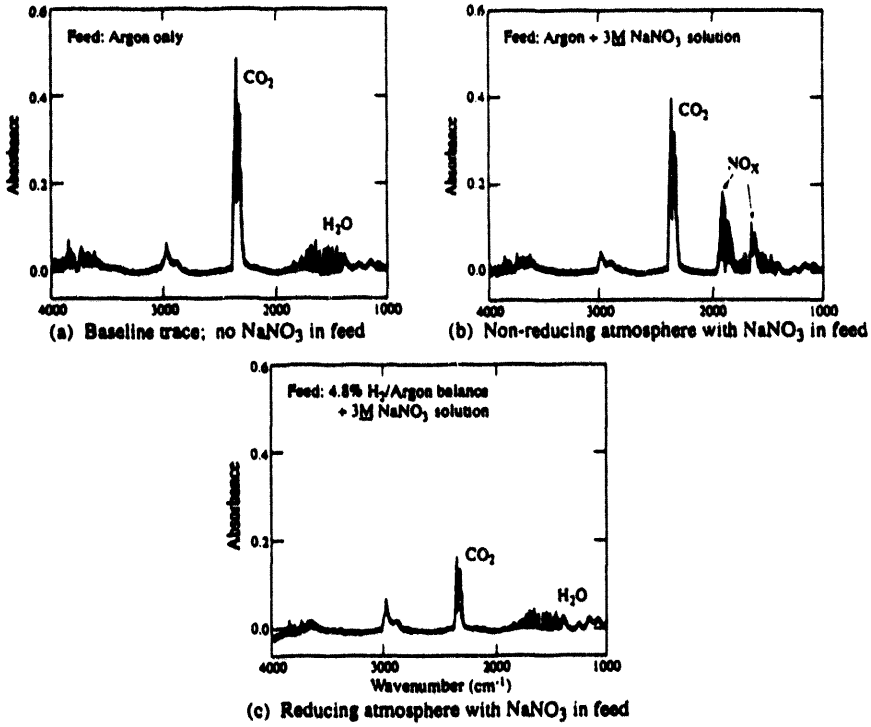

Figure 6. Data demonstrating PBR destruction of Nitrates.

doses in the range 4-7 Mrad (40 - 70 kGy). To better understand the waste removal process and explore e-beam treatment scaling issues, we have employed a computer-based chemical kinetics model to predict the expected removal efficiency and to compare standard electrostatic accelerators to pulsed accelerators in terms of reactive free radical production. Typical measured single-pulse destruction for TCE are in the range 90-95%, in good agreement with our model. We have found that radical production efficiencies are significantly lower for high dose rate than lower dose rates (due to radical-radical recombination). However, simulations of pulse-profile effects indicate that a suitable application of repetitive, short-duration pulses (e.g., 10 kHz, 100 ns) gives radical concentrations and organic removals similar to a DC dose (Table 1).

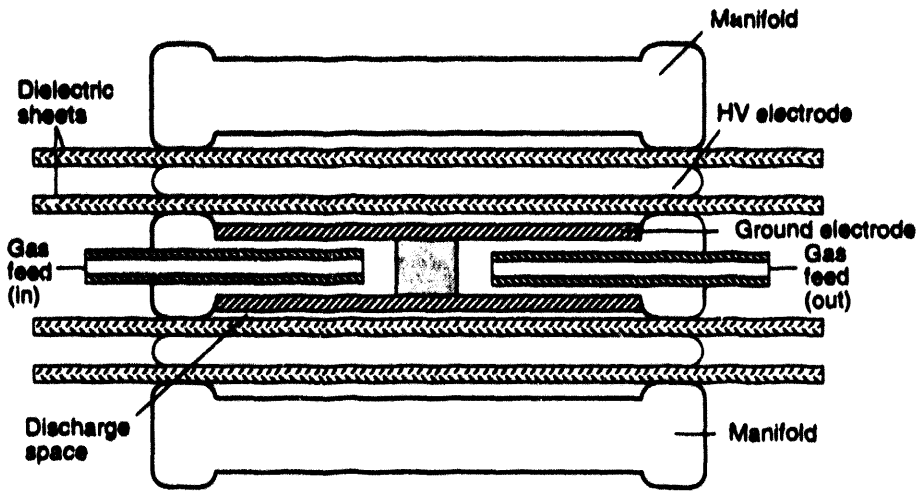

Figure 7. Schematic of existing stacked SDP module containing four planar cells, operating in parallel.

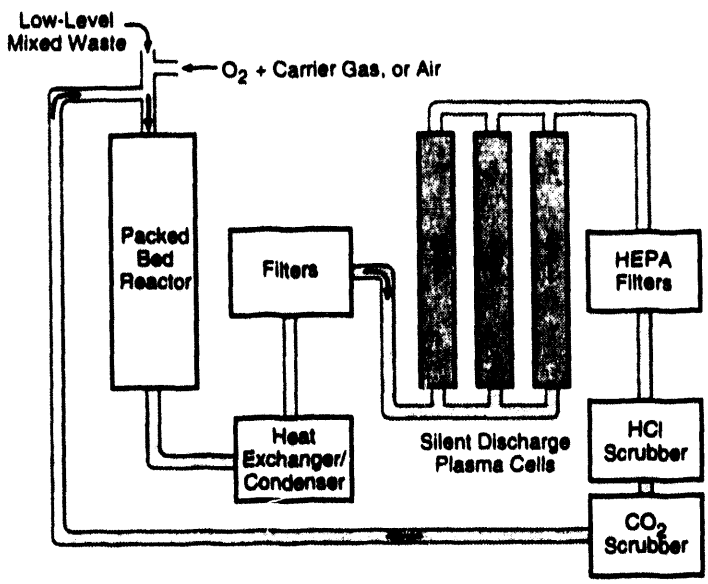

Figure 8. Proposed closed-loop system for treating mixed wastes.

Recent technology developments have lead to a new generation of pulsed linear induction accelerators driven by solid state electrical power conditioning elements. These are considered to be less expensive per unit delivered e-beam dose, physically smaller, modular, and more reliable than conventional electrostatic accelerators. It is speculated that these repetitively pulsed accelerators, developed by industry and the national laboratories, will produce better chemical destruction as well, although this remains to be demonstrated. At present, we have found no data comparing waste destruction by repetitively pulsed accelerators with that of conventional electrostatic accelerators. Once demonstrated these new accelerators would allow a considerable simplification in treatment plant architecture.

Table 1: TCE destruction calculated for different doses and methods of application.

Dose Method	Fractional Destruction (%)	
	100-krad dose	150-krad dose
100-ns pulse	37.5	46.1
1-kHz pulse train	68.0	92.2
10-kHz pulse train	68.8	95.9
DC	69.4	96.8

Notes: initial TCE concentration is 100 ppm; residence time is 0.1 sec.

Potable water or natural water normally contains radical scavengers (e.g., carbonates) that decrease the average radical concentrations and consequently decrease the destruction efficiency. To reproduce the results from the Florida facility, our initial concentrations had to be increased by a factor of 50 because these calculations were based upon a simple, one-step removal mechanism and did not include radical scavenging effects. We have modified our model to account for radical scavengers and more complete destruction mechanisms for TCE and CCl_4. Figure 9 shows the remarkable agreement between model and experiment. This will be particularly important for real wastes (both mixed and otherwise) that will contain scavengers like nitrate and carbonate.

For mixed-waste applicability, we can get some guidance from recent electron-beam irradiation experiments on high carbonate/hydroxide-containing simulants carried out at Sandia (9). In these studies, it was found that, using a high instantaneous dose rate, the percentage of organic carbon in simulated mixed waste sludge decreased by more than 40% for a cumulative dose of 400 Mrad. Preliminary data from radiolytic experiments carried out on simulants characteristic of real Savannah River wastes by our Florida International University collaborators also show that benzene, phenol, nitrobenzene, and 4-nitrophenol can be removed to a relatively high degree by modest irradiation doses (<800 krad). These results are encouraging in showing promise for the treatment of real mixed wastes by electron beams. A general survey of the literature also shows that it may be possible for electron-beam irradiation to play a role in the removal of heavy metals from aqueous solutions, as the solubility of Cd, Cr, Cu, and Zn are significantly reduced under modest irridation.

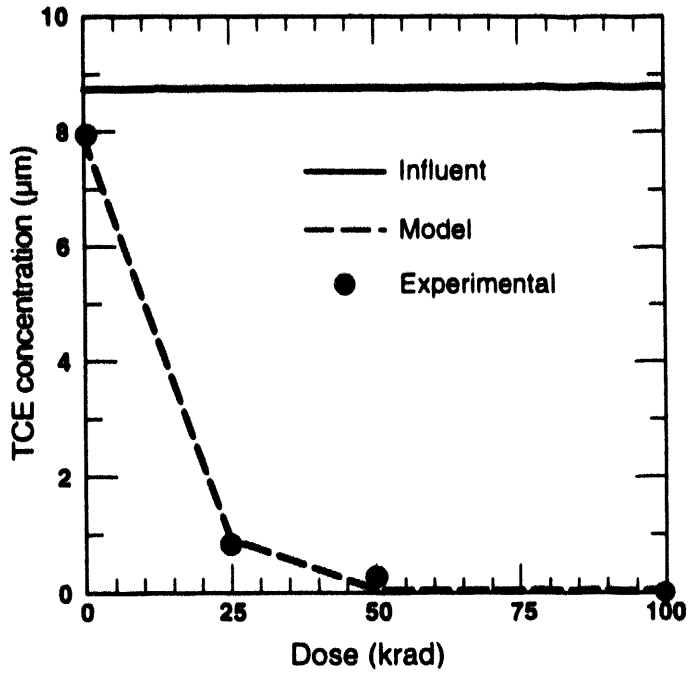

Figure 9. Comparison of model and experiment for e-beam irradiation of TCE contaminated water.

CONCLUSIONS

Closed-loop systems offer definite advantages for treating mixed wastes. Radiolytic treatments are applicable over a wide range of waste streams (liquids, solids and sludges) and the efficacy of silent discharge plasma has been demonstrated, both as a primary and secondary stage, for an expanded list of RCRA and TSCA wastes. An application for an EPA RD&D permit has been submitted to the state of New Mexico for the treatment of LANL wastes using a closed-loop PBR/SDP system. Commercialization of both technologies is promising and industrial CRADAs (with EPRI and others) are being pursued.

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CHAPTER 11

Waste Minimization

U.S. DEPARTMENT OF ENERGY DEFENSE PROGRAMS' APPROACH TO POLLUTION PREVENTION TECHNOLOGY TRANSFER/INFORMATION EXCHANGE

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ABSTRACT. Pollution Prevention can decrease operations costs, lower the volume and toxicity of wastes and improve manufacturing and process efficiencies. In order to ensure that Defense Programs (DP) consistently conducts an effective Pollution Prevention Program, DP has adopted a three-pronged approach to Technology Transfer and Information Exchange.

Defense Programs has developed an information exchange program with industry, academia, and other government agencies to share lessons learned relative to pollution prevention and waste minimization. This program includes aggressive outreach initiatives and benchmarking efforts. Secondly, DP is conducting awareness training and technology workshops that provide practical information on the positive alternatives to treatment and disposal. In addition, a quarterly newsletter is circulated to nearly 2000 recipients inside and outside the Department. Thirdly, DP has also made significant strides in improving operating practices so as to preclude the generation of waste in weapon component production. Many technologies developed at the National Laboratories have already been introduced into industry through technology transfer forums.

INTRODUCTION

The Department of Energy (DOE) recognizes that national priorities are changing because of a changing world political structure and has joined with the public and academia in a collaborative effort to solve the nation's environmental problems. Department of Energy's Waste Minimization Crosscut Plan (1) including the Secretary of Energy Notice 37-92 (an implementing guideline for the Crosscut Plan signed in May), and the Secretary's Policy on Waste Minimization and Pollution Prevention are the most recent indications that DOE supports waste minimization/pollution prevention as a viable means of reversing the trend of environmental degradation. Department of Energy's DP is one DOE office that is affected by the Department's commitment to a pollution prevention approach. Defense Programs also believes in the policy and is the first office to have developed a Pollution Prevention Strategic Plan (2) to implement that policy.

Whereas activities at DP National Laboratories and Production Facilities were for years cloaked in secrecy (open discussions relative to materials and processes were not allowed), the current challenge is to exploit any and all means of communication to the fullest extent possible in the efforts to find solutions to environmental problems. An important part of this communication is providing good information to U.S.citizens regarding DOE plans to prevent additional insult to the environment. This presentation to this audience today is an example of DP's Outreach Program. Before discussion of DP's various modes of information transfer, it may be worthwhile to look into the "scope of work" addressed by pollution prevention/waste minimization initiatives.

Defense Programs is concerned that neither the public nor the Congress may understand the need for and application of waste minimization within the Nuclear Weapons Complex and its application(s) to the private sector. Some have questioned the significance of the term "pollution prevention" when the weapons production system is nearly dormant. Defense Programs feels it is important that the public understand that dismantlement of this system will generate large volumes of material that is no longer serving its original intended purpose. In fact, two important milestones under the pollution prevention objective in DOE's Five Year Plan for FY 1994-1998 (3) are completion of the Weapons Dismantlement Program Strategic Plan and determination of all regulatory requirements for treatment and disposal of weapons components. Some of the discarded material will become hazardous waste, some will become radioactive waste, and some of the byproducts of dismantlement will contain both hazardous and radioactive components thereby becoming "mixed" waste. All of these have associated fiscal and environmental costs. However, radioactive mixed waste, regulated under the Resource Conservation and Recovery Act (RCRA) and under the Atomic Energy Act of 1954, is of special concern because of the land disposal restrictions (LDRs) storage prohibition. The situation is aggravated by DOE's No-Rad Added policy which states that hazardous wastes released from DOE facilities must have no potential to have radioactivity added from DOE activities. Therefore, a great deal of hazardous waste must now be classified as mixed waste and is not allowed off-site for treatment or disposal.

Recovery and reclamation during dismantlement and during ongoing processes will reduce the volume of hazardous, radioactive or mixed waste, and will reduce the need for production or purchase of some quantity of new stock. Recovery, reclamation, and recycling [considered an aspect of pollution prevention by DP, if not by the U.S. Environmental Protection Agency (EPA)] are activities that are typically applied to the retrieval and/or reuse of some material or product that has already been used. For example, the expense associated with the production of enriched uranium has been one incentive for tracking and salvaging uranium from the medium that it may have contaminated. Similarly, many photographic laboratories now try to recover the silver from spent solutions before disposal of those waste streams.

Recovery, reclamation and recycling can be applied to materials other than manufacturing byproducts. The DOE has numerous desks, computers, chairs, file cabinets, laboratory equipment and so forth that are being stored indefinitely because they are not "pedigreed." Application of the No-Rad Added policy dictates that these items cannot be released because there is no proof that absolutely no radioactivity has been added to the items during their use at DOE sites. The public should know that waste minimization/pollution prevention can be applied to materials and processes at sites throughout the Complex that could become something other than "waste" if the proper approach is defined and implemented.

Another area for the application of waste minimization/pollution prevention techniques and technology is that associated with legacy wastes, the result of 50 years of nuclear weapons development and production. Methods must be found to separate hazardous materials from nonhazardous materials, to convert hazardous materials into less hazardous forms, and to identify acceptable long term hazardous material storage techniques.

Finally, waste minimization/pollution prevention will be considered in the design of any new processes, facilities or future reconfiguration of the Nuclear Weapons Complex.

Recognizing that pollution prevention can decrease dismantlement, operations, maintenance and (ultimately) remedial action costs by lowering the volume and toxicity of wastes and improving manufacturing and processing efficiencies, DP is actively addressing the above problems via the aggressive implementation of a Waste Minimization/Pollution Prevention Program throughout the Weapons Complex. One important part of this program is a three-pronged Technology/Information

Exchange Program that supports the Pollution Prevention effort. This three-pronged approach consists of: Benchmarking, Information Exchange, and Technology Transfer.

BENCHMARKING

The routine exchange of information and techniques (both within the Department and between DOE and outside Federal and public entities) promotes a quick response to new and innovative ideas so that no organization has to start from ground zero on each waste minimization idea. A successful Benchmarking Program enables an organization to determine if its program is moving forward or is at a standstill. Priorities may then be modified as appropriate.

Since the private sector was subject to regulation under RCRA nearly four years before DOE was required to comply with the act, DP considered that U.S. industries may be willing to share "lessons learned" during their efforts to minimize regulated activities (and costs) by minimizing waste. Information of this nature is an excellent tool in helping to significantly reduce the time necessary for development and analysis, technical and economic evaluations, prioritization, and implementation of any proposed pollution prevention activity.

One year ago, DP established a Benchmarking Team that reviewed pollution prevention practices with representatives from Imperial Chemical Industries (ICI) Americas, the Rohm and Haas Company, Aluminum Company of America (ALCOA), and Delmarva Power Company. The Team identified numerous business and process practices that were common to all of the companies, then compared these practices. The report on this latter tour was issued in January of this year by DOE Defense Programs.

One result of the benchmarking efforts is that information from the private sector spanning a wide range of subject-related topics has been made available to interested and involved parties at DP National Laboratories and Production Facilities. The benchmarking report is included in training manuals that are distributed to the senior and mid-level DOE managers and DOE contractors who participate in the Pollution Prevention Workshop. The information is also distributed to DP's designated managers for specific waste streams that are generated throughout the Complex. The report is a living document that is reviewed and improved upon by the managers who have the authority to apply the information it contains. Future revisions of the Benchmarking Report will include a lessons learned section and updates on current pollution prevention efforts.

Another positive result of personal interviews with representatives of private industries is that contacts were established at the companies that were visited by the Benchmarking Team. Representatives from companies that were benchmarked participated in the DP-sponsored Pollution Prevention and Integrated Technologies Workshop that was held in March in Santa Fe, New Mexico. The Benchmarking Team discovered that the individuals who have developed and implemented effective pollution prevention programs are interested in seeing their "tried methods" applied at other suitable sites. One company went so far as to allow DOE wholesale use of their own waste minimization plan. Another offered software that had been developed in-house for managing environmental information.

INFORMATION EXCHANGE

To foster the development of the waste minimization program, DP has addressed the need for pollution prevention awareness by conducting pollution prevention workshops and training for DOE and DOE contractor senior management. The half-day workshops include a manual that covers implementation of a waste minimization program and discussion of the leadership required to keep it effective. The manual also provides a summary of environmental regulations that are affected by or that mandate waste

minimization. Additionally, the economic, legal, and social incentives for waste minimization/pollution prevention are outlined. Appendices to the manual constitute other vehicles for information exchange:

- Model Process Waste Assessment Plan
- Model Waste Minimization Plan
- Waste Minimization Contact List
- "Benchmarking Report"

Defense Programs is also conducting biannual Technology Workshops that provide practical information on the positive alternatives to treatment and disposal. Pollution prevention opportunities are identified and stimulating technical papers on dual-use technologies are presented in these workshops, which are offered not only to DP personnel but to anyone in DOE as well as several invited participants from the private sector and academia.

Defense Programs publishes a quarterly newsletter, the *Pollution Prevention Advisor* (4), that highlights DP initiatives in the area of pollution prevention, recent rulemaking, and case studies from industry. The publication is distributed to DOE and DOE contractor employees, to Members of Congress, and to other interested parties in EPA, Industry and Academia.

Defense Programs personnel participated in the "Waste Minimization and Pollution Prevention" Video Conference produced by the University of New Mexico's College of Engineering and the Waste-Management Education and Research Consortium. This eight-program series began in March, 1992 and concluded in October, 1992. The series was honored at TeleCon XII by being awarded the "Best Distance Learning Program for 1992 Higher Education - Live Programming" from the United States Distance Learning Association. Each four-hour program provided interactive satellite television courses focused on waste minimization, including demonstrations of technology for accomplishing waste minimization and discussions of regulations related to waste minimization. With a strong emphasis on technology transfer, each program offered four to six presenters. Defense Programs personnel presented two segments titled, "Why Minimize Waste" and "Process Waste Assessments in the DP Complex."

In 1988, the DOE established the Waste Reduction Steering Committee (WRSC) comprised of members from most of the DOE program secretarial offices (PSO) and cochaired by DP and Environmental Restoration and Waste Management (EM). The WRSC provides a comprehensive approach to pollution prevention within the DOE. Through their site visits to DOE facilities, members of the Committee were able to gather and disseminate ideas that promote pollution prevention awareness and benefits within DOE.

Information exchange is being emphasized in the area of radioactive mixed waste through DOE strategies to comply with the Federal Facilities Compliance Act of 1992. Although the Act requires that DOE submit only a final site treatment plan for review and approval, DOE intends to provide two interim versions of the plan to facilitate discussions between the site and the regulatory agency and among the States, EPA, and other interested parties on technical and equity issues. The interim plans will also facilitate information exchange among the sites and regulatory agencies and will help identify common technical problems and needs. The interim plans will provide information about the technology needs, existing and planned treatment facilities, and treatment options, with each version containing increasingly complete and detailed information.

Defense Programs is convinced that it is important to publicize progress in the field of waste minimization and pollution prevention. To this end, DP has published articles and presented papers that describe the development and implementation of the office's pollution prevention program. This information transfer to other offices in DOE and to other Federal agencies, as well as to the public,

invites comment and feedback. Publicity provides the opportunity for DP to ascertain the degree of the *perceived* effectiveness of its waste minimization/pollution prevention programs and the need for this information in the private sector.

TECHNOLOGY TRANSFER

The DOE and other Federal agencies, including EPA and the Department of Commerce, are working toward the goals of cleaning up the environment and improving the manufacturing competitiveness of our country. DOE perceives the importance of technology transfer and has unequivocally stated that technology transfer is an important part of doing business in the future.

The Department of Energy recognizes that its National Laboratories and Production Facilities possess a vast amount of technical talent and information useful for improving the competitiveness of American Manufacturing. In a joint Memorandum of Agreement (MOA) between DP and EM, the two parties agreed to jointly fund pollution prevention research and demonstration projects within the DOE. (Environmental Restoration and Waste Management and DP are the major stakeholders in this process as DP and EM are waste generators and EM is chartered to clean up and dispose of the waste.) To carry out these activities, the Waste Minimization Management Group (WMMG) was chartered and established within the DOE Albuquerque Operations Office. The primary responsibility of the WMMG was to formulate and implement a complex-wide program to address waste and hazard minimization at the front end of a process from design through production and retirement. Within the DOE, the following nine waste streams were identified: solvents, polymers, plating, miscellaneous, plutonium, uranium, tritium, energetic materials and mixed wastes. A waste stream manager was appointed for each waste stream and was charged with the responsibility of ensuring that the research and development activities address ways for the plants and laboratories to reduce hazardous materials and minimize waste. As part of this initiative, DOE has taken a systematic approach to pollution prevention by prioritizing chemicals with the highest volume usage and toxicity characteristics at all of its production plants. On the nonnuclear production side of DOE, the WMMG has focused on the reduction of solvents such as chlorinated hydrocarbons (CHCs) and chlorofluorocarbons (CFCs); plating chemicals such as hexavalent chromium, cadmium, and cyanide; and polymers such as toluene diisocyanate and 4,4'-methylenedianiline. The WMMG uses technical waste stream managers within the Weapons Complex to guide developments and ensure proper emphasis on projects. Through teamwork and integrated approaches, this group has made significant technical inroads into complex DOE-wide pollution prevention issues.

Many of the technical accomplishments in the area of waste minimization and pollution have been described in the WMMG's recently published *Waste Minimization Program Accomplishments.* This report has the same circulation as the *Pollution Prevention Advisor* and is one of DP's primary vehicles for technology transfer. As with the newsletter, contacts' names are listed under articles and readers are encouraged to write or call with comments or questions on respective topics.

The technology being developed in the Nuclear Waste Complex by DOE or in conjunction with private companies in many cases is applicable in the commercial sector. By teaming with other organizations through a variety of cooperative programs, technology is shared. In some cases, research and development has addressed specific commercial environmental pollution problems. For example, under the Technology Transfer Program, the WMMG waste stream managers receive requests for help that they direct to the appropriate contractor. In one example, small manufacturers were helped to eliminate the use of ozone-depleting 1,1,1 trichloroethane solvent previously used in cleaning medical instruments. In another case, waste stream managers are helping a company to convert to the use of a low VOC paint system and are developing the process for using sprayable powder coatings. One small manufacturer has requested assistance with setting up a new cleaning line that will use aqueous cleaning in place of trichloroethane, a suspected carcinogen. The DOE production facilities are working with various

National Institute of Standards and Technology-funded Technology Centers throughout the country providing training and seminars covering various technologies of interest to small and medium manufacturers. (For example, in August, 1992, AlliedSignal Engineers from DP's Kansas City Plant teamed with Lawrence Livermore National Laboratory to present a seminar on solvent substitution for cleaning. This program, originally broadcast in California, will soon be broadcast to all Technology Centers throughout the country.) Technology transfer is occurring in many forms including direct technical assistance, seminars, workshops, video training, published articles and pamphlets, and training.

An integrated demonstration project of Environmentally Conscious Manufacturing (ECM) was sponsored by the WMMG. This project was a joint effort of Sandia National Laboratories/Albuquerque and the Kansas City Division of AlliedSignal. Environmentally Conscious Manufacturing is essentially designing the hazardous materials out of a product and the processes that produce that product. With ECM, waste minimization and pollution prevention are considered up-front in the product conception phase. In order to minimize waste and prevent pollution, concurrent engineering with design labs must be employed at product inception. Product design, raw materials and process selection, design for dismantlement and recycling are all key issues in ECM. In the joint Sandia/Kansas City project, an electrical subsystem was selected for the ECM demonstration. Processes that produced hazardous waste, that used suspected carcinogens, that polluted the air, that depleted the ozone layer or that were simply inefficient because they produced excessive waste, were not considered supportive of ECM. Engineering drawing and production work instructions were used to identify eight materials and processes which fell into the category of non-environmentally conscious. Six of these materials and/or processes were replaced by environmentally conscious materials and processes. At the conclusion of the production run of twenty-two electrical units, the waste generated using the "standard" manufacturing operation was compared to the waste generated using ECM. The results were dramatic! Environmentally Conscious Manufacturing significantly reduced the amount of waste and pollution. In addition to the reduction of waste, this project illustrated the importance of getting up-front commitment to ECM. Real-world evaluation and feedback was necessary to assure the efficacy and practicality of the chosen alternatives to the "tried and true" operations. Therefore, the project also demonstrated the value of technology and information exchange among individuals from a variety of backgrounds who are focused on the same objective, namely pollution prevention.

CONCLUSION

Defense Programs still has as its primary mission the responsibility of ensuring national security through nuclear deterrence. However, shifting priorities are reflected in shifting funds and, at this time, the EM budget exceeds the budget for defense spending. The most sensible way to minimize environmental impact is to stem or reduce the sources of contamination. Personnel resources are available, in the form of highly trained research scientists, process engineers, technicians, and operators (to name but a few) who can help find alternatives to processes and materials that pose unacceptable human health or ecological risk. Facilities and equipment are also available for demonstrations of innovative waste minimization technologies. Defense Programs is poised to explore new avenues internally at the same time it is seeking direction from academia and the private sector. Defense Programs is also ready to share findings with other interested parties. While DP expends considerable effort in outreach and technology transfer to U.S. industries, it attempts to maintain the momentum within the Department with aggressive advertising of the benefits of waste minimization. Defense Programs recognizes that commitment at every level of the organization is the key to success in its pollution prevention program(s). This commitment is encouraged by DP Senior Management's recognition that pollution prevention is the hallmark of future environmental policy and their relentless efforts to incorporate pollution prevention into everyday operations.

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MIXED WASTE AND WASTE MINIMIZATION: THE EFFECT OF REGULATIONS AND WASTE MINIMIZATION IN THE LABORATORY

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ABSTRACT. The Hanford Site is located in the State of Washington and is subject to state and federal environmental regulations that hamper waste minimization efforts. This paper addresses the negative effect of these regulations on waste minimization and mixed waste issues related to the Hanford Site. Also, issues are addressed concerning the regulations becoming more lenient. In addition to field operations, the Hanford Site is home to the Pacific Northwest Laboratory which has many ongoing waste minimization activities of particular interest to laboratories.

BACKGROUND: THE CHANGING HANFORD MISSION

The Hanford Site was acquired by the federal government in 1943. For more than 20 years, Hanford Site facilities were dedicated primarily to the production of plutonium for national defense and the management of the resulting wastes. In later years, programs at the Hanford Site were diversified to include research and development for advanced reactors, renewable energy technologies, waste disposal technologies, and cleanup of contamination from past practices.

The U.S. Department of Energy (DOE) has established a new mission for Hanford which includes:

- Waste Management of stored defense wastes and the handling, storage, and disposal of radioactive, hazardous, mixed, and sanitary wastes from current activities.
- Environmental Restoration of approximately 1,100 inactive radioactive, hazardous, and mixed waste sites and about 100 surplus facilities.
- Research and Development in energy, health, safety, environmental sciences, environmental restoration, waste management, and national security.
- Technology Development of new environmental restoration and waste management technologies, including site characterization and assessment methods; waste minimization, treatment, and remediation technology; and education outreach programs.

Facilities at the Hanford Site are no longer in a production mode. Wastes generated on the Hanford Site come from past practices and current research efforts.

THE REGULATIONS: HOW WASTE MINIMIZATION SUFFERS

Speculative Accumulation: Enforced by the State under RCRA

The Dangerous Waste Regulations in the State of Washington are codified in the Washington Administrative Code (WAC) (1). The WAC regulates speculative accumulation by limiting the amount of time a waste may be stored. There are situations in which a waste that is generated could be used or recycled further down the road, but because of the speculative accumulation period, it must be disposed of. By regulating waste in this manner the statute forces a generator to create waste instead of allowing the generator to re-use or recycle.

More specifically, if a material is identified as a speculatively accumulated material, i.e., no use or method of recycling has been identified for the material within the calendar year, the material is classified as a solid waste and is subject to Resource Conservation Recovery Act (RCRA) storage restrictions. Therefore, unless a use or method to recycle the material is immediately available, the material automatically becomes waste.

Under WAC (1) a material is:

> "accumulated speculatively if it is accumulated before being recycled. A material is not accumulated speculatively if it can be shown that the material is potentially recyclable and has a feasible means of being recycled and that during the calendar year . . . the amount of material that is recycled equals at least 75% of the amount of material accumulated at the beginning of the period."

As written, speculative accumulation does not provide for unique materials such as radioactive contaminated shielding, which could be re-used, but not always within one year. According to the statute, if the shielding is not reused or recycled within one year, it must be disposed of as waste. This puts the DOE in the unique position of generating radioactive mixed waste without being in a production mode.

As an example, facilities at the Hanford Site that have been shut down and stand to be decommissioned use large amounts of lead shielding to protect workers from exposure. The decommissioning process, which is an emerging technology, involves timely procedures for securing required permits, ensuring proper reviews, getting adequate funding, etc. Before decommissions can begin, most of the lead shielding will have been disposed of as hazardous or mixed waste because of the speculative accumulation regulations. It simply is not feasible during the decommissioning process to devise within one year a re-use or recycling procedure for lead shielding.

As a result of the speculative accumulation requirements, new lead will have to be procured for shielding purposes because the previously used lead had to be disposed of as waste, needlessly generating additional hazardous or mixed wastes. If lead could be stored until it was needed for shielding, instead of disposing of it as waste, a substantial waste minimization savings could be realized.

Derived-From Rule

The derived-from rule (1) prohibits any action to evade the intent of the regulation by dividing or diluting wastes to change their designation, except for the purposes of treating, neutralizing, or detoxifying such wastes.

In effect, this increases the amount of waste generated if there should be any dilution of a waste stream other than for the purposes of treatment, neutralization, or detoxification by characterizing the entire stream as waste. In addition, WAC (1) stipulates that if a non-hazardous waste stream is contaminated

with a "dangerous waste source" waste stream (waste codes F001-F024, K001-K087, and W001), the entire waste mixture is designated as hazardous waste.

This could mean that if one molecule of the regulated hazardous waste gets into a non-regulated waste stream, the entire stream, including any piping or equipment associated with the stream, becomes a regulated hazardous waste.

It would be ideal if waste constituents could be separated and the amounts of these constituents isolated. However, for large facilities such as those at the Hanford Site, it is not always possible to keep particular constituents separate. The derived from rule, therefore, will always act to increase the volume of waste in a stream that has some hazardous waste constituents.

Liabilities if Waste is "Sold"

Large amounts of wastes and excess chemicals are generated at the Hanford Site which could be recycled or reclaimed. Many of these materials are recycled by off-site vendors. The Hanford Site, being a government-run facility with "deep pockets", must be extremely cautious in who it contracts with to recycle/reclaim materials. If the recycler should ever dispose of hazardous wastes improperly, the DOE could become partly liable for clean-up of the waste because of RCRA Cradle-to-Grave liability.

It often takes a year or more to select a vendor for recycling hazardous materials from the Hanford Site. This time is spent auditing and verifying that the vendor is performing its work within federal, state and local laws. After a contract is established, if the "integrity" of the vendor is ever questioned, the contract is not renewed and the selection process starts again. During the time the selection of a vendor is in process, recyclable waste continues to be generated at the site. The generated waste must be disposed as hazardous waste within 90 days of generation because of the regulations prohibiting "speculative accumulation". Much waste that could be recycled ends up being disposed of as hazardous waste.

Recyclable materials generated in radiologically controlled areas pose the same problems as above, with the added concern of being potentially contaminated. Particularly troublesome are lead acid batteries, lead metal (bricks, sheeting, blankets, shot, etc.), and mercury which are all good radiation shields. Health physics technicians are reluctant to unconditionally release these items offsite because they may be "shielding" internal contamination. The generators end up disposing of the materials as mixed wastes. This issue concerning release from radiologically controlled areas has contributed to hampering waste minimization efforts at the Hanford Site. In certain situations, even packing material surrounding equipment that was taken into one of these areas could not be released and was disposed of as radioactive waste. Simple solutions such as unpacking equipment outside of the control area have been implemented. Hopefully, release procedures and control measures can be improved so that waste minimization efforts may prevail.

HOW THE REGULATIONS MAY BE CHANGING

The U.S. Environmental Protection Agency (EPA) recently issued a proposed rule "Hazardous Waste Management System; Modification of the Hazardous Waste Recycling Regulatory Program" (2).

Under the proposed rule, certain post-user items that are usually managed as hazardous wastes (e.g., used batteries and suspended/canceled pesticides) could be collected and handled under less stringent requirements. It would appear that EPA's intent is to encourage proper treatment and/or recycling of these wastes, and further facilitate separation of these wastes from the municipal waste stream.

Specifically, EPA refers to these post-user types of wastes that will be subject to less stringent requirements as "universal wastes" and identifies certain common characteristics they share. These characteristics include:

- frequently generated in a wide variety of settings other than industrial settings usually associated with hazardous wastes;
- generated by a vast community, the size of which poses implementation difficulties for both those who are regulated and the regulatory agencies charged with implementing the hazardous waste program; and
- may be present in significant volumes in the municipal waste stream.

It would appear, therefore, that if a waste can be characterized as a "universal waste", the waste would be subject to less stringent requirements, possibly allowing more opportunities for recycling or re-use. This, however, is only a proposed rule and if promulgated does not necessarily have to be implemented by those states granted RCRA authority by the EPA.

WASTE MINIMIZATION INITIATIVES AT THE HANFORD SITE

Co-Disposal

Co-disposal is an innovative waste minimization technique being developed at the Hanford Site. Co-disposal involves using existing solid and liquid wastes, instead of clean materials, as fill material in radioactive and mixed waste landfills and trenches. This material is referred to as "waste rock".

These existing wastes, including soil washing sludge, contaminated soils, demolition rubble, fly ash, purge water, leach water, etc., would ordinarily need to be disposed of separately. Co-disposing of these wastes in landfills and trenches, rather than using clean material, saves the funds required to dispose of these existing wastes and avoids the creation of new waste from the clean materials.

The innovation of the Co-disposal project is that waste is treated as product to dispose of other waste (Figs. 1 and 2). It is estimated that Co-disposal will increase landfill capacity from 100% to 300% over traditional landfill use.

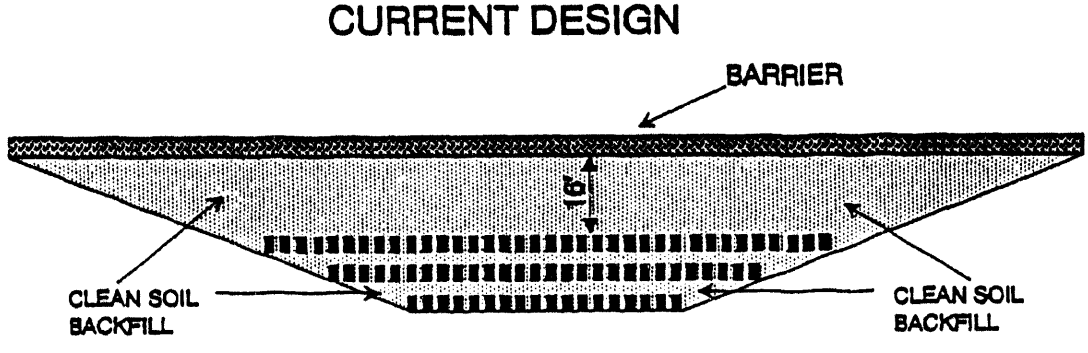

Figure 1. Co-disposal: wasterock replaces clean soil (current design).

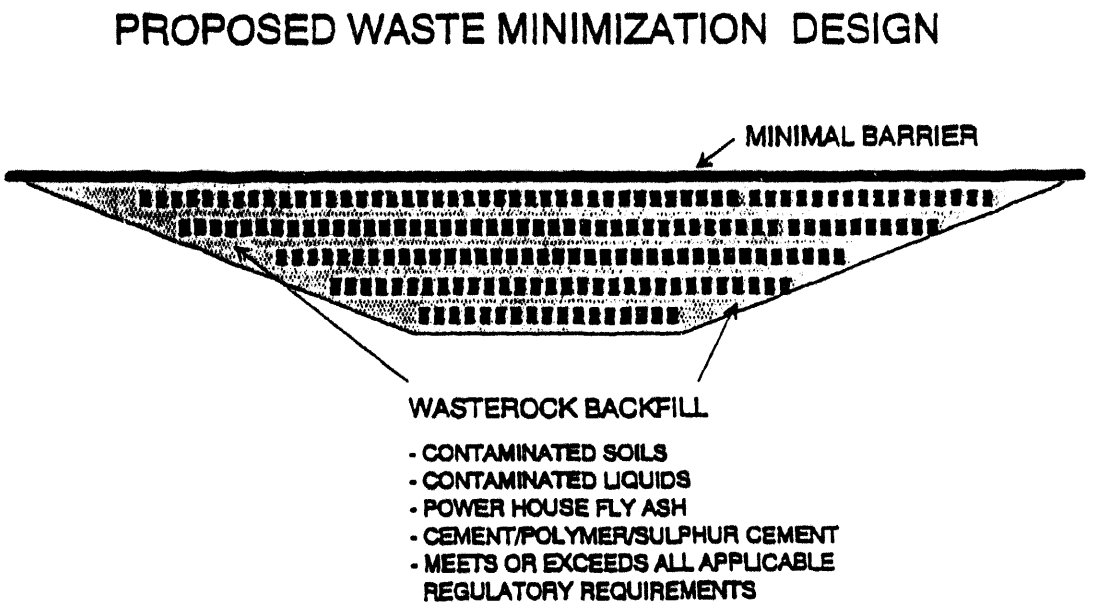

Figure 2. Co-disposal: wasterock replaces clean soil (proposed waste minimization design).

Surplus Property Management

Contaminated tools and equipment that are no longer needed are given to other on-site facilities to use. Many of these items have rough or porous surfaces, or inaccessible areas which cannot be surveyed properly. If another facility can use the material, disposal and replacement costs can be reduced. Some examples of "recycling" excess contaminated materials at Hanford are:

1. Contaminated handtools from shutdown production reactors (100-Areas) were given to 200-Area process facilities and waste management facilities.

2. Railroad ties and telephone poles from stabilized waste sites were given to tank farms for use as vehicle stops in radiologically controlled areas.

3. Chain-link fencing that surrounded contaminated or hazardous waste sites was removed when clean-up was completed. The fencing could not be economically released as free of radioactive contamination. Instead of disposing of the fencing as contaminated waste, the fencing was installed around active burial grounds.

WASTE MINIMIZATION IN THE LABORATORY: PACIFIC NORTHWEST LABORATORIES

Pacific Northwest Laboratory (PNL) operates facilities located on the Hanford Site and is under contract for Research and Development to the Department of Energy, Richland Field Office (DOE-RL). Pacific Northwest Laboratory is divided into different research centers (Centers), each providing expertise in areas of science and engineering. For example, the Materials and Chemical Sciences Center performs research in the area of physical, chemical, and radiochemical analysis techniques, while the Earth and

Environmental Sciences Center performs research with regard to groundwater modeling, lysimeter research, and the effects of hazardous and radioactive substances on microbial environments.

Pacific Northwest Laboratory provides research support on various DOE-sponsored and non-DOE-sponsored work.

WASTE GENERATION

The following is a brief list of research projects PNL is currently involved in and the wastes they generate. All of these programs generate mixed waste to some degree. Efforts to seriously curtail mixed waste generation and to eliminate it if possible are underway.

Vitrification Technology

Research is being conducted on vitrification technology wherein solid and/or liquid radioactive wastes are placed inside a controlled environment (a melter) along with frit material and superheated until the waste mass is turned into a glass-like material. This material is impervious to groundwater leaching, weathering, etc. A counterpart to melter technology is In-Situ Vitrification wherein plots of soil in the environment are superheated to form this glass-like material. This program generates Low-Level Radioactive waste (LLW), mixed waste, and hazardous waste. The mixed waste generated under this program usually consists of soils contaminated with heavy metals and organics as well as liquids contaminated with same.

Groundwater Program

This program area consists of modeling the groundwater beneath the Hanford Site, as well as lysimeter research to investigate transfer rates of various substances through the soil column. Mixed waste generated from this program consists of radioactively contaminated liquids, sampling and analysis wastes (including scintillation counting wastes), and chemical reagent wastes from laboratories.

Fuels Research

Another program in which PNL is involved is research into nuclear fuels. Hot-cell facilities are used to investigate the properties of various materials when irradiated. Mixed wastes generated from this program consist of grinding and polishing solutions containing methanol and perchloric acid with a high degree of radioactivity. Another mixed waste stream generated by this program is solvent contaminated rags from the cleaning of hot-cell manipulator parts.

Tank Core Characterization Program

Pacific Northwest Laboratory provides a great deal of research support to the Tank Core Characterization Program. The Hanford Site is the home of 28 Double Shell-Tanks (DSTs) and 149 Single-Shell Tanks (SSTs) used for the storage of high-level radioactive wastes generated from the reprocessing of spent nuclear fuel during the Manhattan Project. A program is in place to characterize the contents of these tanks. Westinghouse Hanford Company (WHC) (the Management and Operations contractor at the Hanford Site) is responsible for sampling the tanks and shipping the sample material to PNL for analysis. Pacific Northwest Laboratory receives the samples into various hot-cell facilities located in the 300 Area and performs physical, chemical, and radiochemical analyses. Since PNL is heavily involved in this area with many Centers participating, this program generates a large amount and wide variety of wastes. The various solid and liquid wastes generated from this research are very high in radionuclide activity. Low-level wastes and mixed wastes are the prevalent waste streams.

WASTE DISPOSAL

DOE-generated mixed wastes have two potential disposal pathways:

Disposal to the Radioactive Liquid Waste System

Five PNL facilities in the 300 Area of the Hanford Site are connected to a WHC facility (also in the 300 Area) via underground pipeline. Liquid mixed wastes and LLW that meet certain criteria may be disposed of to the Radioactive Liquid Waste System (RLWS). The liquid wastes are received at the WHC facility (340 building) and stored in two 10,000 gallon underground storage tanks. When tanks near their capacity or the 90-day clock is approaching, the tanks are pumped into a 20,000 gallon rail car and transported to the 200W area for disposal into the DSTs. This disposal pathway is currently operated at no cost to PNL other than staff time. Therefore, there is incentive to determine if a mixed waste meets the criteria for disposal to the RLWS. In some cases, neutralization scenarios can prepare a mixed waste for RLWS disposal, thus saving the cost of disposing to the Central Waste Complex.

Disposal to the Central Waste Complex

If mixed waste does not meet the criteria for disposal to the RLWS, it must be packaged into drums and shipped to the Central Waste Complex located in the 200W area and operated by WHC. Mixed waste is stored at this facility for future treatment. The one-time cost for transportation and storage of a 55-gallon drum is approximately $2,000. This cost, coupled with the extensive paperwork and staff time involved in disposal provides great incentive for minimizing mixed waste streams.

WASTE MINIMIZATION PROGRAM AT PNL

Current Tasks

PNL's waste minimization program is still in its adolescent stage of development. Process Waste Assessments (PWAs) have been performed on 5 recurring waste streams out of the Craft Services Department. The waste streams assessed were batteries, fluorescent light tubes, fluorescent light ballasts, paint wastes, and waste oils. In addition, the research centers have developed waste minimization plans which are reviewed annually. Pacific Northwest Laboratory provides data for inclusion in annual site-wide waste minimization reports (3-5).

Future Tasks

DOE has provided some funding for 1993 for the following tasks:

1. Develop a database to track all waste generation (LLW, mixed waste, transuranic (TRU), hazardous wastes) across PNL.

   This database is in the early stages of development. Databases currently exist for these waste streams and a centralized database is being developed that will import data from them. There is also the possibility of compatibility with the Chemical Management System (CMS). The CMS is a PNL-wide database system in which research staff log in the chemicals that they are using in their laboratories. In the future, the centralized waste database could be linked up with the CMS and with the database system that Procurement uses. The entire chemical management process, from purchasing to disposal, could then be tracked together allowing for greater implementation of waste minimization strategies.

2. Develop generator-specific waste minimization training.

   Currently, waste minimization training is one module in the Hazardous Waste Generators Training program. General waste minimization objectives and goals are presented in this class as well as techniques that can be employed to meet the objectives. Through the use of the above waste generation database, waste minimization training will be developed for each facility and will be generator-specific. For example, training in waste minimization techniques relating to paint use and solvent cleaning will be developed and presented to Craft Services staff. Waste minimization techniques related to sampling and analysis procedures will be developed and presented to various research staff involved in these areas. Waste minimization training given in this manner will ensure that specific techniques are implemented in the field in applicable areas rather than general techniques being implemented for all staff. As a result, waste minimization accomplishments will increase.

3. Develop a waste minimization incentives program to stimulate research staff in the area of waste minimization technologies.

   This task involves developing a program that provides funding for waste minimization technologies to be applied in research applications. One idea is to organize a contest in which research staff submit technologies that would aid in minimizing their wastes. The staff submitting the technology that has the best cost/benefit ratio would receive funding to purchase the technology. Examples include: a scintillation counter that requires less cocktail per sample, vial crusher/extractor, and others.

WASTE MINIMIZATION SUCCESS STORIES

There have been specific waste minimization techniques implemented within the last two years at PNL that have resulted in significant waste reduction and cost savings.

Product Substitution

Generation. PNL routinely uses scintillation cocktails for counting radioactivity in SST/DST core samples and other radiochemistry efforts at the Hanford Site. Older cocktails contained xylene, toluene, methanol, and pseudocumene, all of which are regulated as hazardous wastes and are flammable, creating a fire hazard and limiting storage capabilities within the laboratories. The use of these cocktails generated mixed waste which costs approximately $\$200.00/ft^3$ to dispose of (a 55-gallon labpacked drum would therefore cost $1,500.00).

Product Substitution. Two new non-regulated scintillation cocktails were evaluated: Ultima Gold and Opti-Fluor. These cocktails do not contain RCRA or State-regulated constituents and therefore do not result in mixed waste generation. Normally, these wastes would be absorbed onto diatomaceous earth and disposed of as LLW (at the cost of approximately $500.00 for a 55-gallon drum). However, these waste cocktails fit the criteria for disposal to the RLWS and thus, disposal cost nothing. Other benefits besides cost savings include safer working environment due to non-flammability, no 90-day clock or satellite accumulation regulatory issues, and less staff time spent on disposal (paperwork, labeling, inspection, etc.).

Cost Savings. As a result of product substitution, approximately 350 gallons/yr of mixed waste was not generated. This resulted in a cost savings of $26,000.00.

Waste Reduction Combined with Product Substitution

Waste Generation. Research staff were using a regulated scintillation cocktail in a liquid scintillation counter that used 20 ml vials per sample. This generated a significant amount of mixed waste requiring disposal at approximately $200.00/ft^3 (a 55-gallon labpacked drum would therefore cost $1,500.00).

Waste Reduction/Product Substitution. PNL research staff investigated the use of 7 ml vials in place of the 20 ml vials and confirmed that this would not require a new scintillation counter (special carriers would be used) and this switch would still produce statistically valid sample results. This resulted in a 3:1 reduction.

Then, the staff switched to Ultima Gold, a non-regulated scintillation cocktail thus ceasing the generation of mixed waste.

Finally, the staff researched and purchased a liquid scintillation counter that uses plates instead of the 7 ml vials. Each plate has 96 wells and each well uses 0.2 mls cocktail. This resulted in a 35:1 reduction.

Cost Savings/Benefits. Total waste reduction from 20 ml vials to .2 ml wells per sample is 100:1 reduction. The cost savings amounts to approximately $12,000/yr in disposal costs alone.

Benefits include: vastly decreased staff time spent on disposal paperwork/handling, much greater numbers of samples can be run during a single counting, flammability hazards of cocktail have been removed by switching to non-flammable cocktail, and much less liquid wastes are handled thus reducing the hazard of radionuclide contamination.

This waste minimization activity is unique in that the staff combined two waste minimization techniques and thus produced a hundred-fold reduction. Combining of waste minimization techniques should be investigated in all waste minimization scenarios.

Product Substitution

Waste Generation. Research staff were using 1,1,1-Trichloroethane with rags to clean manipulator parts for use in hot cells. This activity resulted in approximately two drums of mixed waste per year.

Product Substitution. Staff investigated and confirmed that switching to a non-hazardous degreaser was feasible.

Cost Savings. Implementing this waste minimization technique eliminated the generation of two drums of mixed waste per year resulting in cost savings of approximately $2,500.00/yr.

SUMMARY

The current state and federal environmental regulations important to activities at the Hanford Site were not originally promulgated with waste minimization in mind. It is important to seek changes in this area so that reuse and recycling opportunities can be administered.

Waste minimization is a rapidly developing area and one of vital environmental importance. It not only applies to large operating facilities, but to laboratories and small quantity generators as well. As the

waste minimization program at PNL continues to grow, waste generation should decrease significantly thus saving time, money, and effort while making the workplace safer for PNL staff.

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ISSUES FACING THE MANAGEMENT OF RADIOACTIVELY CONTAMINATED LEAD WITHIN THE DOE SYSTEM

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ABSTRACT. The purpose of this paper is to discuss and evaluate the issues that managing and operating contractors in the U.S. Department of Energy (DOE) system should consider that are associated with management of radioactively contaminated elemental lead. There are many instances where DOE contaminated lead fall within Resource Conservation and Recovery Act (RCRA) regulation. In light of the Federal Facilities Compliance Act (FFCA), it is becoming increasingly important for additional regulatory options to be explored in order to facilitate proper treatment, storage and disposal of RCRA regulated lead.

Various DOE facilities have initiated processes to reuse or recycle contaminated lead. Technologies such as melt-refining, surface blasting, and electromigration are being explored. One or more of these technologies may be the key to reducing contaminated lead inventories in the DOE system. Many DOE facilities are finding that these efforts need to have stringent regulatory evaluation since some alternatives have proven to be environmentally desirable but not economically feasible.

There is not a single answer to addressing the issues associated with contaminated lead in the DOE system. However, many DOE facilities have taken significant steps to manage their lead. It is extremely important that various factors are considered when identifying the proper management, use and disposal of contaminated lead.

INTRODUCTION

The advent of the Federal Facilities Compliance Act (FFCA) of 1992 (PL 102-386) has required the Department of Energy (DOE) system to take another look at its mixed waste generation, inventories and compliance status. The FFCA defines "mixed waste" as, ". . . waste that contains both hazardous waste and source, special nuclear, or by-product material subject to the Atomic Energy Act of 1954." The DOE complex is required to submit various inventory and mixed waste treatment reports to Congress and the States over the next few years. Also, the FFCA provides an incentive for the DOE complex to negotiate site specific compliance agreements and orders to facilitate the management of mixed wastes. If DOE is successful, it will preserve its sovereign immunity under Resource Conservation and Recovery Act (RCRA) and avoid some of the harsh implications of the Land Disposal Restrictions (LDRs) storage prohibition. Therefore, to facilitate RCRA LDR compliance, DOE is re-evaluating its strategies for storage, treatment and disposal of these wastes.

Historically, the DOE system has preferred to use lead for the purposes of shielding in its nuclear reactors, hot cells and laboratory processes. As a result, a portion of the mixed wastes reported for the FFCA includes significant volumes of radioactively contaminated lead. As of the date of this paper, the FFCA information was not finalized. However, according to the October 1991 DOE Land Disposal Restrictions Case By Case Extension Application for Radioactive Mixed Wastes, an estimated 958 m^3 (~24 M lbs) of mixed lead waste has been generated in the DOE complex. The annual generation rate for DOE

contaminated lead is approximately 112 m^3 (~2.8 M lbs). These figures suggest that many opportunities still exist for the development and implementation of more aggressive waste minimization strategies to reduce the inventory of lead in the DOE system and for management to more aggressive steps towards treatment.

The FFCA amended RCRA. Ever since the RCRA was promulgated in 1976, industry and government have been faced with of the task of developing new technologies and management strategies to maintain compliance with hazardous waste regulations. An additional twist in the management of hazardous waste has resulted from energy research and energy production involving nuclear reactor operations and from nuclear weapons development, in which hazardous wastes are contaminated with radionuclides. Unfortunately, mixed wastes were not addressed when RCRA was first enacted. In particular, "mixed waste" has posed special management challenges for government agencies such as the Department of Energy (DOE) and the Department of Defense (DOD). This paper will discuss the issues and management strategies that are currently being addressed to facilitate the proper storage, treatment and disposal of radioactively contaminated lead shielding (such as lead bricks, sheets and blankets) in the DOE system.

CHARACTERIZATION

As mentioned above, there are many activities involving radioactivity in the DOE system that require shielding. Historically, lead was the predominant material for this purpose. Elemental lead's chemical and physical properties make it extremely useful for shielding as part of ongoing efforts to keep personnel exposures "as low as reasonably achievable." As various nuclear facilities are decontaminated and decommissioned (D&D) or sites remediated under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the clean-up activities may generate lead. RCRA regulates "solid wastes" which are also "hazardous." Sometimes it is problematic to determine when something is only a "solid waste" versus a "hazardous waste" or, not a "waste" at all as the following situations will illustrate.

Scenario 1

Some facilities automatically declare their radioactively contaminated elemental lead shielding as RCRA regulated mixed waste. Their facility does not have another use for the material. Also, the facility is unable to decontaminate the lead shielding for release and use outside the DOE system. As a result, because the material is being discarded, contains lead above the RCRA characteristic limits, and is radioactive, the facility would probably characterize this wastestream as a "mixed hazardous waste" and must follow all applicable RCRA regulations applicable to storage, treatment and disposal.

Scenario 2

Sometimes lead shielding can be re-used in other processes at a facility. For example, lead bricks from the D&D of an older facility may be used as shielding in a hot cell in an operational facility. In this case, the lead shielding would not be considered "waste" (and, therefore, not a "solid waste") since the shielding is not being "discarded." (1) Therefore, the lead shielding would not be subject to full RCR A Subtitle C requirements.

Scenario 3

There are situations where the radioactive component can be separated from contaminated lead and, as a result, the lead may be eligible for recycling. For example, cnce the lead is decontaminated it may be eligible for "free release" outside of the DOE system for recycling in smelters; or, the radioactively contaminated lead could be melted and used as lining material for low level radioactive waste containers.

In this case, similar to Scenario 2, the lead shielding would not be considered a "solid waste" since it is being re-used for its intended purpose; or, when used as a material for a protective liner, is being made into a product (1).

As one may see, when lead shielding can be re-used or recycled it is no longer a "waste" and can be excepted from full RCRA Subtitle C regulation. Some of this lead would be considered recyclable "scrap metal." RCRA defines scrap metal as, ". . . bits and pieces of metal parts (e.g., bars, turnings, rods, sheets, wire) or metal pieces that may be combined together . . . which when worn or superfluous can be recycled." (1) This designation would require compliance with Section 6.2, "Radiological Survey, Sampling, and Analysis," of EM-30's "Performance Objective for Certification of Non-Radioactive Hazardous Waste," dated October 16, 1991. This lead can be stored for recycling provided that 75% (by weight or volume) is recycled during the calendar year (1). It should be noted that if a facility manages its lead shielding as a recyclable material, it must ensure that their claim that this material is not a "solid waste" is documented pursuant to (1). Specifically, the facility must demonstrate that there is a known market or disposition for the material and that the facility meets the terms of this exclusion. The facility must provide appropriate documentation to demonstrate that the material indeed is not a waste.

However, as noted, there are instances when lead shielding cannot be re-used or recycled. For example, some facilities do not have a use for additional lead; furthermore, off-site release may not be a management option because the lead cannot be decontaminated to off-site release levels. As a result, the facility may have to characterize and manage this lead as RCRA regulated mixed waste. In this instance, there are special management problems since there are few commercial facilities whose waste acceptance criterias permit the treatment or disposal of radioactively contaminated hazardous waste.

It is evident that it is extremely important that a facility properly characterize its wastes. For example, transportation requirements will differ depending upon whether or not one is shipping hazardous or nonhazardous waste. Once a material is characterized as "waste" a facility is subject to various requirements relating to the material's proper storage, treatment and disposal. Furthermore, if the facility is handling RCRA regulated wastes it must ensure that all persons involved in the management of this waste are properly trained.

TREATMENT STANDARDS

Standards and Definitions

In order for a RCRA regulated hazardous waste to be land disposed, it must meet the LDR exit criteria for the hazardous constituents it contains. RCRA entrance and exit criterias are not always identical. In some cases, the exit criteria is much more stringent than the entrance criteria. The objective of the land disposal restrictions is to ensure that particular hazardous wastes are subject to specified levels of treatment to substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste so that short term and long term threats to human health and the environment are minimized (2).

Unlike some regulated wastes, lead shielding has a very specific LDR treatment standard. It is a technology based standard versus a concentration based standard. Table 3 of 40 CFR 268.42 (3) identifies lead shielding as being subject to treatment as a "radioactively contaminated lead solid." The treatment standard [or "best demonstrated and available technology" (BDAT)] for radioactive lead solids is "MACRO" or "macroencapsulation." As a result, if lead shielding is macroencapsulated then a facility may certify the waste pursuant to 268 and send it for disposal to a RCRA Subtitle C facility. (Remember, however, that if radioactively contaminated lead shielding is macroencapsulated it must be finally disposed at a facility that holds approved permits to accept both hazardous and radioactive wastes.)

When a facility meets the technology based LDR treatment standard for contaminated lead solids it is not rendering the waste nonhazardous. It is only reducing the mobility, leachability and toxicity of the waste being treated. As a result, the final waste form and treatment residue are still RCRA regulated until it can be proven that these waste forms are no longer hazardous. Since "lead" is a characteristic, not a listed waste, delisting is not an option for the waste to be excepted from Subtitle C regulation. However, a facility may perform Toxicity Characteristic Leaching Process (TCLP) analysis on the final waste form. If the final waste form passes TCLP then exception from Subtitle C regulation may be an option. As noted in the introduction, there are few facilities that can accept wastes that are regulated by both the AEA and RCRA. However, once the lead meets its LDR BDAT, it may be returned to RCRA TSD storage. In this situation, there is no time limit within which this waste must be sent for final disposal.

Radioactively contaminated lead is not "debris," nor "inherently hazardous debris." In the August 18, 1992 rulemaking finalizing the debris treatment standards, EPA specifically excepted from the definition of debris those wastes which already had a specific treatment standard provided in (3). As mentioned above, the LDRs have very specific treatment standards for radioactively contaminated lead solids. As a result, even though the waste form of contaminated shielding is identical or similar to other wastes considered as debris, EPA found that certain wastes, such as the D008 radioactively contaminated lead solids, should be treated according to their existing LDR treatment standards. Note, however, that at certain points in its management cycle, such lead can be managed as "debris" if it has been radioactively decontaminated. In this case, the lead could be managed as "inherently hazardous debris" since it would be "itself hazardous because it is fabricated with toxic constituents" and would not have a specific treatment standard. However, as in the case with radioactive lead that is recycled, lead that is considered inherently hazardous debris that was also scrap metal being recycled would not be subject to the land disposal restrictions.

RCRA Permitting Requirements for Treatment

RCRA defines treatment as, ". . . any method, technique, or process, including neutralization, designed to change the physical, chemical, or biological character or composition of any hazardous waste so as to neutralize such waste, or so as to recover energy or material resources from the waste, or so as to render such waste nonhazardous, or less hazardous; safer to transport, store, or dispose of; or amenable for recovery, amenable for storage, or reduced in volume (8). A facility must have authorization in its Part A or a Part B permit to perform a specific treatment for a specific waste code. If a specific treatment is not listed on the facilities RCRA permit (or application) for a particular waste code, the facility may ask EPA/RCRA Authorized State for a change to the permit. In the alternative, a generating facility may treat contaminated lead, as it is being generated, in a 90 day area, such as in a tank, container or containment building. A generator is not required to obtain a RCRA permit for this type of treatment (5). However, the generator must prepare and follow a written waste analysis plan pursuant to (4). This, of course, does not mean that the generator may not be subject to other environmental permitting requirements.

Note that if a facility is recycling its lead then it may proceed with decontamination and other activities to recycle the lead without worrying about a RCRA permit. Since the material is not a "waste" in this situation, RCRA permitting requirements do not apply. However, the facility may need to obtain other permits or authorization for their activities (i.e. , NEPA, NESHAPS, NPDES, etc.)

Alternatives to BDAT for Lead

If a facility feels that an alternative treatment technology is more appropriate, it could petition the (RCRA) Authorized State or EPA region, whichever is appropriate, for a treatability variance; or, the facility may decide to perform RCRA treatability studies to investigated the viability of an alternative treatment process. However, RCRA treatability studies may never be used as a mechanism to commercially treat or dispose of hazardous waste (4). For lead solids that are generated as a result of CERCLA activities, a CERCLA treatability study may be appropriate in instances where the waste form poses unusual problems for

treatment or there is a question as to the performance standard of the preferred technology. Many facilities, such as the Idaho National Engineering Laboratory, are pursuing options such as these to facilitate the treatment of lead solids in the DOE system.

TREATMENT ALTERNATIVES AND TECHNOLOGIES

Macroencapsulation of Lead Solids

Lead waste and lead treatment residuals which are in the solid form can be isolated from the environment by using macroencapsulation. Macroencapsulation is the process of coating waste with a polymeric substance or an inert inorganic material to encase the waste and thus minimize the potential for harm to the environment. EPA recommends macroencapsulation as the BDAT for the treatment of radioactive lead solids which will ultimately be land disposed. This standard does not include treatment residuals that can be stabilized using pozzolanic processes (6).

The macroencapsulation process consists of four steps. The first step will involve sorting lead into recyclable and non-recyclable lead. Only the non-recyclable lead will be macroencapsulated. The non-recyclable lead should then be reduced to a standard size for treatment. In the second step, the lead blocks will be coated with a polymeric material. The polymeric material must be in a liquid form. To coat the block, the block can be dipped into the polymeric material or spray-coated with the material. The third step would allow for cooling and curing of the polymer and inspection of the integrity of the coating. The final step is the packaging and disposal of the waste.

Design parameters include type of polymer, operating temperature, and control of air emissions. Several materials can be used for encapsulation such as asphalt, polyethylene, thermosetting plastics, and resins that can be polymerized in the presence of a catalyst. The choice of material depends on the waste to be treated, and will affect the operating temperature, the selection of equipment, and the curing time. For waste contaminated with alpha and beta radiation, most materials would be effective; however, for waste contaminated with gamma-emitting radiation, many polymers would lose their integrity over a period of time.

TREATMENT: INEL EXAMPLE

The following example illustrates a common circumstance for many DOE facilities and describes the actions taking place at the Idaho National Engineering Laboratory to establish an on-site lead decontamination facility. The purpose for establishing a decontamination facility is to allow removal of the presently contaminated lead from storage as a mixed waste in order to recycle or reuse the lead.

Contaminated lead at the Idaho National Engineering Laboratory

There is approximately 1.6 M lbs of radioactively contaminated lead is stored at the INEL. The lead is in such forms as shielding bricks, casks, sheets, blankets, and shot. The primary radiological contaminants are cobalt-60, cesium-137, and strontium-90. This material is being stored as mixed lead waste subject to the Resource, Conservation, and Recovery Act (RCRA) hazardous waste management regulations (4). Approximately 1.3 M lbs of this lead would be considered available for surface decontamination. In its present form, there is approximately 400,000 lbs of lead shielding bricks and lead sheet of various configurations that would be very amenable to surface decontamination. In addition 900,000 lbs of lead filled casks that have been surface contaminated would also be amenable to surface decontamination. Any lead that is determined to be volume contaminated would not be considered for surface decontamination.

The proposed decontamination facility will provide the capability of meeting the Department of Energy (DOE) waste minimization policy by providing for the decontamination and recycling of lead. Recycling of the lead would reduce the existing volume of waste in RCRA regulated storage and would reduce the need to mine and refine lead-bearing ore to produce additional lead.

The mixed lead waste Contaminated lead is currently being stored at the INEL in compliance with RCRA hazardous waste management regulations which includes the land disposal restriction (LDRs) requirements of (3). The lead was placed in RCRA storage prior to May 8, 1992, which means that the LDR storage prohibition does not apply. But, the other requirements which became effective for mixed waste under (3) that restrict generation and require specified treatment technologies and/or standards still apply to these materials prior to land disposal.

Since the Federal Facility Compliance Act (FFCA) of 1992 requires federal facilities to identify "a plan for developing treatment capacities and technologies for treatment of all mixed wastes, regardless of the time they were generated..." it would seem prudent to be actively pursuing available treatment technologies to remove minor surface decontamination.

The decontamination facility being developed, includes decontamination technologies for the many forms of lead that are contaminated on the surface with minor amounts of radioactive isotopes. A facility of this type, which is to be utilized for decontamination would be subjected to a NEPA evaluation.

Resource, Conservation, and Recovery Act

RCRA standards for this decontamination activity are proposed based on the interpretation that the mixed waste lead would be designated as a recyclable material under (1). The recyclable material designation would be based upon the ability to provide sufficient evidence that the decontaminated lead is destined for a bona fide end use. Although it would be still considered a hazardous waste, the mixed waste lead would be exempt from many requirements of RCRA. RCRA regulations provide this exemption in order to encourage recycling and allow treatment of materials that would otherwise be designated as hazardous waste.

Residuals from the decontamination process would be stabilized in Department of Transportation (DOT) approved 55 gallon drums for disposal at the Radioactive Waste Management Complex (RWMC) in accordance with the RWMC waste acceptance criteria.

In order to verify that the decontaminated lead is free of radiological contamination, each piece would be surveyed to ensure that the surface decontamination meets the unrestricted release limits of DOE Order 5400.5 and a high percentage of those pieces would be sampled to ensure that lead is not volume contaminated.

Depending upon the decontamination technology used there is the potential that with some processes, airborne particulates may be generated during the decontamination procedure. Appropriate respiratory protection and clothing must be used. Negative air pressure would be required for the facility and HEPA filtration would be used to contain any airborne contamination. The required Air permits must be obtained. In most cases, existing facilities already have existing air permits to conduct the type of activity described.

Residual from decontamination with liquids

Where decontamination processes use liquids to remove external contamination, a stabilization process would be required to treat the residual to a form that would pass the Toxicity Characteristic Leaching Procedure (TCLP) test prior to disposal. Disposal of non-RCRA regulated low-level waste would occur at RWMC subject to the facility's waste acceptance criteria.

STORAGE

Regulatory Background

The LDR storage prohibition states that the storage of hazardous waste is prohibited unless the storage is solely for the purpose of the accumulation of such quantities necessary to facilitate proper recovery, treatment or disposal (6). In this context, a facility is given a period of up to one year from the date of waste generation by EPA to properly dispose of its hazardous wastes. After this time, the facility has the burden to prove that it is storing these wastes for permissible purposes. However, hazardous wastes placed into storage prior to their effective date are not subject to the storage prohibition until the wastes re-trigger the LDR standards (such as by "placement" on the land). A certain percentage of the DOE lead in storage falls into this category. Lead, D009, is a "characteristic" of hazardousness that falls into the third/third hazardous waste category. Furthermore, this waste type, lead shielding, is more often than not managed as "mixed waste." The effective date for such wastes was May 8, 1992. EPA did extend the effective date one year for third/thirds contaminated debris and mixed wastes by approving a national case-by-case (CBC) extension due to lack of available treatment capacity (7). Later, EPA also extended the effective date to May 8, 1993 for mixed soils for the same reason (7). (DOE headquarters did submit its own DOE complex-wide CBC petition pursuant to (3) for the purposes of requesting additional time to develop and implement treatment for its radioactively contaminated third/thirds wastes. Lead was listed as one of the wastestreams to be considered in the CBC petition. DOE stated that much of its third/thirds wastes are amenable to the same treatment as its solvent and California list wastes. However, DOE was prioritizing the treatment of solvent and California list contaminated wastes because their effective dates had already passed and much of these wastes are subject to the LDR storage prohibition. To date, EPA has not acted on this request in part because of the passage of the FFCA.

IMPORTANCE OF STATE INVOLVEMENT AND THE EFFECT OF RCRA AUTHORIZATION

There are DOE operations in states that only have authorization for the "base" RCRA program. In states where this is the case, if they have not been granted interim or final authorization for mixed wastes, mixed wastes are not regulated in that state. However, if this state is shipped to another state where mixed wastes are regulated, then what was once unregulated becomes subject to all applicable regulations in the receiving state. This issue can be crucial consideration as facilities consider whether or not to ship their wastes to another facility for treatment, storage or disposal.

It is extremely important to ensure that appropriate management personnel are working with the State regulators. In some instances, early information and notification to the State about a planned project can avoid unnecessary delays and eliminate options which appear viable but are impermissible or too costly under state law.

LEAD MANAGEMENT

Management Strategies

As the above issues illustrate, being successful in managing radioactively contaminated lead can be difficult. Prospectively, it makes sense not to generate any additional contaminated lead unless it can be recycled or treatment is available. By adhering to this ideal, a facility can limit its potential RCRA liability. There are many mechanisms being used in the DOE complex to make success in mixed waste management not only viable but possible. The following items represent some of the tools that the various facilities in the DOE complex have used in their waste management process.

Aggressively Promoting Pollution Prevention

Various environmental regulations, including RCRA, embrace the philosophy of waste minimization and pollution prevention. As illustrated above, a facility can save dollars by preventing the generation of contaminated lead by source reduction and material substitution at the beginning of the project. Many facilities have instituted strict controls and procedures to prevent the unnecessary procurement of clean lead. Also, several facilities are looking at other materials, such as concrete, as viable alternatives for shielding. Other facilities are coating their lead prior to use so that only a small layer of the brick is contaminated. At the end of the process, some DOE facilities are looking at alternative treatment technologies to reduce the volume of waste generated from the treatment process. All of these things can reduce the facilities cost of compliance and final disposal for contaminated lead.

However, instituting an effective pollution prevention program can be challenging. EPA has published several guidance documents on waste minimization. However, many professionals in the field agree that the elements of a successful program include: top management support, clearly defined project scope and objective, accurate waste and cost accounts, and technology transfer.

Closely Tracking LDR Compliance and Mixed Waste Generation

Tools such as roadmaps have become a mechanism of choice to identify issues, guide and plan waste management for DOE environmental restoration and waste management activities over the past several years. Roadmap documents are developed through a very systematic planning process that focuses on issue identification, root cause analysis and issues resolution. For example, the INEL drafted and finalized an LDR roadmap to assist the facility in addressing LDR compliance concerns. This roadmap included mixed wastestream information from all of the INEL contractors. It identified desired activities for issues resolution and Activity Data Sheet integration, and included a comprehensive LDR issue resolution analytical tree and implementation plan. It is expect that roadmapping will play a significant role in the development of the DOE complex-wide National Compliance Plan.

Another mechanism by which to track mixed waste compliance is to require additional management involvement in the process. Some facilities have instituted programs whereby any mixed waste to be generated must receive management approval prior to generation. In this review process, management looks at various factors such as, necessity of generation for health and safety purposes, possibility of material substitution, and availability of treatment, before she decides to approve generation. After the waste is generated, management is kept informed about the wastes generation rates, management and arrangement for final disposal. Also, the facilities are surveilled to ensure adherence to the process. Early management involvement can facilitate the procurement of funds and availability of technology to ensure that mixed wastes that are generated have treatment available.

Using NEPA to Facilitate Your Program

In order to meet the intent of the National Environmental Policy Act (NEPA) of 1969, and its substantive goals for environmental protection, contractors to the Department of Energy are required to begin decisionmaking and planning for each project by completing an environmental checklist prior to the initiation of any work. An Environmental Checklist describes specific the nature of the work performed, details surrounding the proposed activity and identifies the environmental laws and regulations potentially applicable to the proposed activity. Once the Environmental Checklist has been completed, the activity is evaluated to determine the level of environmental assessment necessary to ensure harmony between man and his environment.

CONCLUSION

Successful management of contaminated lead in the DOE system can be a challenging project. However, knowledge of the regulations, proper planning, and top management support can facilitate the approvals necessary to achieve treatment and final disposal of this material. Roadmapping, training, pollution prevention, and team building can assist a facility in re-using, recycling or substituting other materials for contaminated lead shielding. There are many viable alternatives to the LDR treatment standards for contaminated lead. Many facilities are leading the way in changing the culture in which we manage our mixed wastes.

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DECONTAMINATING LEAD BRICKS AND SHIELDING

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ABSTRACT. Lead used for shielding is often surface contaminated with radionuclides and is therefore a Resource Conservation and Recovery Act (RCRA) D008 mixed waste. The technology-based standard for treatment is macroencapsulation. However, decontaminating and recycling the clean lead is a more attractive solution.

Los Alamos National Laboratory decontaminates material and equipment contaminated with radioisotopes. Decontaminating lead poses special problems because of the RCRA hazard classification and the size of the inventory, now about 100 metric tons and likely to grow substantially because of planned decommissioning operations. This lead, in the form of bricks and other shield shapes, is surface contaminated with fission products. One of the best methods for decontaminating lead is removing the thin superficial layer of contamination with an abrasive medium under pressure. For lead, a mixture of alumina with water and air at about 280 kPa (40 psig) rapidly and effectively decontaminates the lead. The abrasive medium is sprayed onto the lead in a sealed-off area. The slurry of abrasive and particles of lead falls through a floor grating and is collected in a sump. A pump sends the slurry mixture back to the spray gun, creating a continuous process.

The process generates small volumes of contaminated lead slurry that can be solidified and, because it passes the Toxicity Characteristic Leaching Procedure (TCLP), is not a mixed waste. The decontaminated lead can be released for recycling.

INTRODUCTION

Lead is often used as shield against radiation. At Los Alamos National Laboratory (LANL), decommissioning operations have produced about 50 tons of lead which is surface contaminated with fission radioisotopes, including ^{137}Cs, ^{60}Co, ^{90}Sr, and possibly ^{152}Eu and ^{90}Y. Most is in the form of bricks, although there are also some sheets. Future planned decommissioning operations will substantially increase this inventory.

Radioactive lead is a Resource Conservation and Recovery Act (RCRA) D008 mixed waste. The technology-based standard is macroencapsulation. However, because the Toxicity Characteristic Leaching Procedure (TCLP) test requires that the waste be reduced to pieces smaller than one centimeter, macroencapsulation still produces a mixed waste.

Decontaminating and recycling the lead is, obviously, a much more attractive option. LANL's equipment decontaminates lead by removing a thin superficial layer using an abrasive media of water, alumina, and air. This slurry version of sandblasting is conducted at low pressure and considerably reduces airborne lead and radioactivity. The volume of effluent is minimal and can be rendered nonhazardous.

The equipment is mounted in an enclosed trailer, which can be moved and operated at the decommissioning site to avoid packaging the contaminated lead (Fig.1).

BACKGROUND DATA

In the late 1980s, tests on decontamination of lead were run by a private contractor for the Department of Energy at Oak Ridge National Laboratory (ORNL). Various techniques were tested, including high-pressure wet sandblasting and high-pressure water blasting. However, the low-pressure blasting (210-280 kPa) with a mixture of fine alumina, water, and air gave the best results (Fig. 1). This medium at this pressure is sufficiently abrasive and removes only a few mils of lead; decontamination to releasable limits was easily reached. The abrasive medium was also fully recycled.

One effluent produced is the used alumina--when it has lost its abrasive property--mixed with radioactive lead. During the tests, one 200 liter drum of this waste was produced every three months. Generation rates will vary with the level of use of the equipment, which was not reported, but effluent generation should in any case be low. This effluent was solidified in cement, although it seems that no TCLP was run to determine whether the waste was not hazardous.

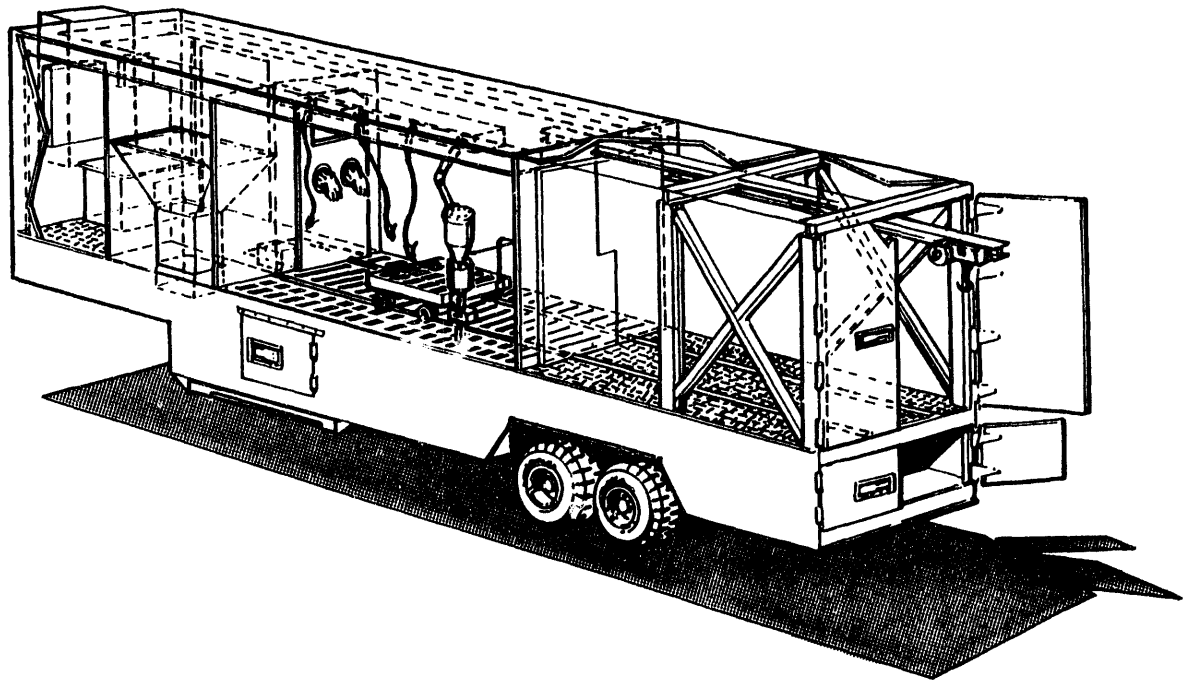

Figure 1. Lead decontamination trailer.

When decontamination is completed, the lead shapes are washed with clean water. This water becomes contaminated with fine lead particulates. Most can be removed by settling and, when filtered through a 1.5m filter, the residual lead concentration was about 0.01 mg/L. Approximately 200 L of this effluent were produced per day.

Decontamination rates ranged from 0.05 m^2/min to 0.2 m^2/min. However, these rates do not include unpacking, staging, surveying the clean bricks, packaging, treating effluents, and maintaining equipment; the actual rate is estimated to be about 0.01 m^2/min of total operating time.

EQUIPMENT DESCRIPTION AND OPERATION

The equipment purchased is a 13.5 m enclosed trailer divided into three compartments.

- The forward control room area, approximately 3.3 m x 2.3 m, which contains electrical controls, operator clothing change area, HEPA filter, and glove ports for decontaminating small parts. The small parts are located in the main blast booth.
- The staging area, about 4.8 m x 2.3 m, located at the rear of the trailer. An overhead hoist can extend 1.2 m beyond the rear bumper on a rolling beam. It has a capacity of two tons. Parts to be decontaminated can be deposited on a cart on rails. This area also has a mixer to mix the sump waste with cement.
- Personnel access the main blasting booth through the control room. Waste on the cart is rolled in from the staging area through two large double doors. The booth is equipped with a deadman blasting gun, breathing air connections, a cyclone to separate the solids from the liquid, a small parts table, a water filter, and push-button controls. The floor is stainless steel grating to let the slurry drain into the sump, which has secondary containment.

The exhaust from all areas is HEPA filtered. Heating and air conditioning provide comfortable working conditions. Walls, ceilings, and floors are made of 304 stainless steel for easy decontamination. Safety features prevent operating the decontamination equipment when the access doors to the blasting area are not hermetically shut or when the room pressure is insufficiently negative.

The slurry of abrasive and water is pumped from the sump by a rubber-lined vertical sump pump to the blasting gun, where it is mixed with compressed air at about 210 to 280 kPa (30 to 40 psig). The gun blast is directed at the piece to be decontaminated. The slurry drains through the grated floor and into the sump and is recycled through the gun. At the end of the decontamination operation, a clean water spray is used to clean up the piece (Fig. 2).

When the abrasive media must be discarded, the slurry is sent through a cyclone which separates the liquid from the solids. The heavy underflow slurry is then mixed with cement in a 115- or 200-L drum using a propeller and an air motor mounted on an air-operated lifter.

The excess water, after being allowed to settle, is pumped with an air-operated diaphragm pump through a 10-m filter and a 1-m cartridge filter and then into a drum. It is then discarded to the Radioactive Liquid Treatment Plant, a wastewater treatment plant that treats radioactive water generated facility wide.

The trailer can be used for decontaminating various low-level contaminated parts and can be moved on-site as long as electric power is available. A skid-mounted electric air compressor and the breathing air unit are also transportable. Small quantities of fresh water must be available.

REGULATORY REQUIREMENTS

When lead can be decontaminated and reused, it is not a waste and is not subject to RCRA regulations such as for storage; and treatment is a recycling operation. There are many potential users for this lead at LANL. When decontaminated to free release, the lead could also be sent to a smelter.

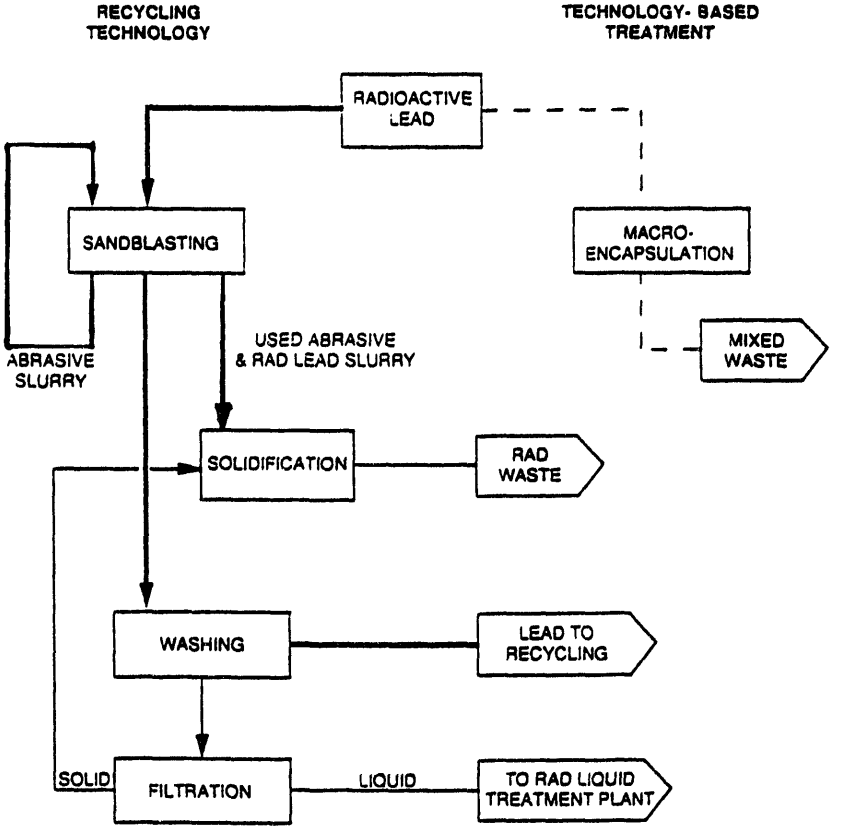

Figure 2. Decontamination and recycyling of lead.

When exhausted, the abrasive slurry is a waste containing radioactive lead. Therefore, it is a mixed waste. Solidification in cement is the technology selected by LANL. However, if the solidified slurry does not pass the TCLP, it still is a mixed waste, and finding a landfill for disposal is difficult. The TCLP, of course, requires the cement to be crushed, which exposes some of the lead. Solidification tests were run at laboratory scale on commercial minus 325 mesh lead powder at various lead-to-mortar ratios. The mortar was purchased premixed. Results are reported in Table 1. Compressive strength of the mortar for various abrasive loadings was also tested (Table 2).

Table 1. TCLP results, mortar without additives

% Pb Loading	0	0.5	1	2	3.75	10	20
TCLP, ppm Pb	0.21	0.35	0.53	1.65	26.3	72.8	134
Non-Hazard	X	X	X	X	X		

Table 2. Compressive strength results.

Grit % wt Loading	0	10	20	40
Compressive strength, PSI	570	990	1010	820

MINIMIZATION OF MIXED WASTE IN EXPLOSIVES TESTING OPERATIONS

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ABSTRACT. In the 1980s, efforts to manage mixed waste and reduce pollution focused largely on post-process measures. In the late 1980s, the approach to waste management and pollution control changed, focusing on minimization and prevention rather than abatement, treatment, and disposal. The new approach, and the formulated guidance from the U.S. Department of Energy, was to take all necessary measures to minimize waste and prevent the release of pollutants to the environment. Two measures emphasized in particular were source reduction (reducing the volume and toxicity of the waste source) and recycling.

In 1988, a waste minimization and pollution prevention program was initiated at Site 300, where the Lawrence Livermore National Laboratory (LLNL) conducts explosives testing. LLNL's Defense Systems/Nuclear Design Program has adopted a variety of conservation techniques to minimize waste generation and cut disposal costs associated with ongoing operations. The techniques include minimizing the generation of depleted uranium and lead mixed waste through inventory control and material substitution measures and through developing a management system to recycle surplus explosives. The changes implemented have reduced annual mixed waste volumes by more than 95% and reduced overall radioactive waste generation (low-level and mixed) by more than 75%. The measures employed were cost-effective and easily implemented.

BACKGROUND

Lawrence Livermore National Laboratory (LLNL) Defense Systems Program research is conducted at Site 300. At the Site 300 firing facilities, we burn or detonate non-nuclear weapons components and materials to verify weapons design and material performance. Prior to 1989, virtually all of the waste generated at the explosive testing facilities, which amounted to approximately 500,000 kg annually, was characterized as mixed waste. Our mixed waste was disposed of in on-site landfills, which were regulated as interim status Resource Conservation and Recovery Act land disposal units (1). In November 1988, this practice was terminated. LLNL management determined that land disposal of our explosive testing facilities' untreated mixed waste was not practicable nor desirable from a compliance perspective. We substituted mixed waste land disposal practices with a commitment to waste minimization, which meant avoiding or reducing the volume of mixed waste generated, and establishing a program to meet the commitment.

PROGRAM ORGANIZATION AND GOALS

In establishing our waste minimization program, we developed an organizational structure for managing and implementing our waste minimization efforts (2). We defined the roles and responsibilities of those involved, and the policies and goals to be instituted. Our management (Defense Systems Program) assigned line responsibility for the development and implementation of the changes to the management of the explosives testing facility. DS management believed that the explosives testing employees, who are familiar

with the materials, processes, and procedures for the operations, were the best resources for identifying areas where waste minimization changes could be made. The Defense Systems Program waste minimization organization is shown in Figure 1.

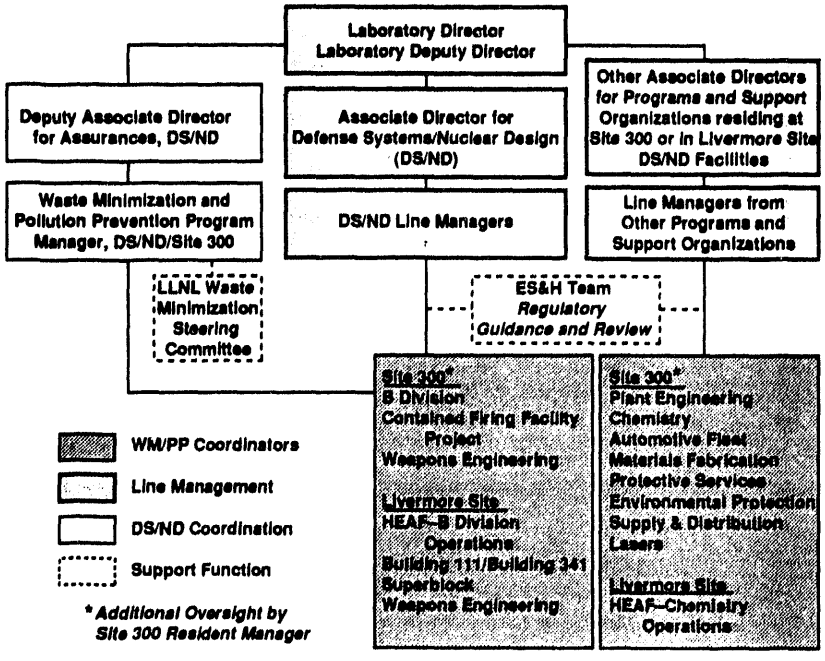

Figure 1. DS/ND WMPP Organization.

Our goal was to reduce the total volume of hazardous and mixed wastes by at least 25% in three to five years, using volumes generated in 1988 as our baseline. We achieved that goal one year later, in 1989, using the methods described below.

WASTE MINIMIZATION METHODS

The first step we took involved developing a detailed characterization of all the materials entering and exiting the explosive testing operation, and identifying all the materials control and waste generation points along the way. We identified five target areas where we believed there were opportunities for waste reduction:

- Several hazardous materials were potential components of experiments, and the various experimenters using them did not have a mechanism for formally declaring that the waste from their test was potentially mixed waste.
- Procedures were not in place to control materials present on the firing table prior to explosives testing and removal of waste materials for disposal.
- Lead used as weights and as shielding material in the operations was largely responsible for the creation of mixed waste from the operations.
- At the conclusion of a number of types of explosive tests, the remains of tents constructed with lumber and plastic were left in configurations that resulted in large volumes of waste with large void spaces.
- Virgin explosives were used for routine maintenance and training operations.

Utilizing this information, we adopted the following hierarchical approach: (1) eliminating or reducing sources of mixed waste by material, process, or housekeeping controls; (2) recycling wastes through reclamation or reuse; or (3) if these two options were not available, arranging for environmentally acceptable waste treatment to reduce the toxicity and/or volume of the mixed waste generated. We used source reduction methods to address the five waste minimization target areas identified below. The specific changes we made in inventory control, explosive test procedures, management of lead, tent construction, and reuse of explosives are described in detail below.

Inventory Control

All Site 300 explosives testing activities are required to have a formal "peer review" accompanied by a completed data base form that describes materials to be used in the test. This data base form, shown in Figure 2, specifically highlights state and federal hazardous constituents which could, if present, cause the waste to be a mixed waste instead of a low-level waste. The data base form has two columns: one column is filled out by the lead experimenter, and the other is filled out by the facility supervisor or designee. The combined information represents the potential wastes to be generated from the experiment.

PLEASE enter weights or volumes in the units called for.

B-DIVISION SITE 300 SHOT DATABASE INFORMATION

>>RAMROD/EXPERIMENTERS: List ONLY materials in the shot assembly that will end up in the bunker waste stream.
DO NOT include material that will be recovered or recycled.
>>BUNKER: List ONLY the bunker-placed materials that will end up in the bunker waste stream.
DO NOT include material that will be recovered or recycled.
>>If this completed form is UNCLASSIFIED, submit it with the Pre-Shot.
If this completed form is CLASSIFIED, submit it appropriately as a Classified Work Paper to Alberta Tracy, L-801.
>>NOTE: Bunker Supervisors MUST be notified well in advance of any experiment containing any materials listed below that are preceded by a bullet (•).

		RAMROD	BUNKER	* (i.e., LX-10, 9404, Comp-B, propellant, etc.)
	Type of experiment* * *		XXXXXXX	* * (and/or compounds)
	Account #		XXXXXXX	
	Bunker Shot #	XXXXXXX		
	Shot Name		XXXXXXX	
	Fire Date	XXXXXXX		
	Ramrod		XXXXXXX	
	Diagnostics >>>>>>			<< DIAGNOSTICS
	Program		XXXXXXX	450 X-Ray X
	Explosive #1 (name)*	XXX		Accelerometers ACC
	Explosive #1 (wt.)	(Kg)		Digitizers D
	Explosive #2 (name)*	XXX		* * * Expmt type: Effects E
	Explosive #2 (wt.)	(Kg)		(choose one) Fabry-Perot I
	Explosive #3 (name)*	XXX		Conventional weapons Flashlamps FL
	Explosive #3 (wt.)	(Kg)		Device hydro FXR F
	Explosive #4 (name)*	XXX		Diagnostic developmen Hycam HC
	Explosive #4 (wt.)	(Kg)		Environmental IC Camera IC
1	Antimony* *	(gm)		HE development Laser Fld LF
2	Arsenic* *	(gm)		Proliferation/NEST Linac L
3	Asbestos	(gm)		SDI Locam LC
4	(•) Barium* *	(gm)		Structural studies Optics O
5	Beryllium* *	(gm)		Surety Pins P
6	(•) Cadmium* *	(gm)		Other (define) Recovery R
7	(•) Chromium IV* *	(gm)		Scopes S
8	(•) Chromium III* *	(gm)		Strain Gauges SG
9	Cobalt* *	(gm)		Thermocouple T
10	Copper* *	(gm)		Video V
11	Flouride Salts	(gm)		
12	(•) Lead* *	(gm)		
13	(•) Mercury* *	(gm)		
14	Molybdenum* *	(gm)		
15	Nickel* *	(gm)		Ramrod name (please print):
16	(•) Selenium* *	(gm)		
17	(•) Silver* *	(gm)		
18	Thallium* *	(gm)		
19	Vanadium* *	(gm)		Ramrod signature:
20	Zinc* *	(gm)		
21	Other lithium salt compounds	(gm)		
22	Tritium (in micrograms)	(ugm)		
23	Thorium* *	(gm)		Bunker Rep name (please print)
24	Uranium* *	(gm)		
25	Corrosives (eg.: acids, bases)	(ml)		
26	Solvents	(ml)		
27	PCB	(ml)		Bunker Rep signature:
	Comment(s)			
	Comment(s)			

Waste Certification Program: Signature:
Print name:
Date:

NOTE: Before table gravel from this shot is loaded into boxes, this sheet must be reviewed and signed by the LLNL Waste Certification Officer or designee.
This signature certifies that the container contents are as reported on this form.
April 93 Issue. Discontinue use of earlier issues.

Figure 2. B-Division site 300 shot database information waste certification form.

Completion of this form before the test encourages one of two results: (1) either non-hazardous constituents are substituted for hazardous constituents or (2) plans are developed to ensure that the waste from the experiment is segregated from other non-mixed waste and is strictly managed as potential mixed waste. This new inventory control process prevents inadvertent hazardous material from entering the wastestream.

Explosives Test Procedures

A detailed procedure was written as a reference and training guide for employees involved in the explosive testing operations (3). The procedure describes potential wastestreams; the steps to be followed in removing, packaging, storing, and managing the waste; and training requirements for handling the waste. The procedure also contains information to prevent removal of excessive amounts of firing table gravel following an experiment.

Management of Lead

We dramatically minimized the generation of depleted uranium and lead mixed waste at the explosive test facilities by (1) substituting nonhazardous steel weights for lead weights in all operations and (2) using aluminum or steel barriers to protect lead shielding from fragmentation. Implementation of these simple, cost-effective measures resulted in savings of approximately $500K after the first year of implementation.

Tent Construction

The design of the tents used to enclose explosives tests was changed from a plastic and lumber tent that generated a large volume, twisted mass to a cloth tent supported by ropes that collapsed into a much smaller volume of waste following testing. Implementation of this measure saved approximately $50K in 1990.

Explosives Reuse

Surplus explosives pieces from other LLNL explosives operations are used in place of new stock explosives for shot evaluations, microbarograph testing, and employee training exercises. A user-friendly on-line computer data base was developed by LLNL to facilitate the use of surplus explosives (4). Users can advertise the availability of surplus explosives, locate sources of needed explosives, and post notices for explosives that are being sought. The surplus explosives are made available to experimenters at no cost. Figure 3 illustrates the types of information provided to users of the data base. The surplus explosives data base system promotes minimization of reactive wastes.

ACCOMPLISHMENTS

When we started our waste minimization program in 1988, our goal was to achieve a 25% reduction in waste volumes within three to five years. We accomplished this one year later, in 1989. Since then, continual improvements have been made to reduce the volume of our explosives testing operations wastestream. As a result of the measures described above, we have reduced the estimated 484,000 kg of mixed waste generated in 1988 to approximately

263,000 kg of low level waste in 1989
141,000 kg of low level waste in 1990
115,000 kg of low level waste in 1991, and finally
72,500 kg of low level waste in 1992.

This represents an 85% reduction in the mixed waste stream since 1989. Throughout this period, the number of explosives tests remained constant, so the reduction cannot be attributed to reduced activity. The

results of our efforts are shown in Fig 4. As of the end of calendar year 1992, approximately $1.6M in mixed waste container purchase, transport, and disposal costs have been avoided as a result of our efforts.

Explosives Inventory Data ID#: _____

Explosive Name: _____

Composition: _____ Quantity: _____ Ogms Olbs Okgs

Form: O*bulk powder* O*pressed* O*cast/cured* O*paste* O*liquid*

Storage Review Date: _____ DOT Shipping Class: _____

Classification (new UN designation, if available): _____

Container: O*plastic* O*glass* O*cardboard* O*other (specify)* _____

Contact: O*Livermore Site* O*Site 300*

Name: _____ Phone: _____ FAX: _____ L-Code: _____

Description/Special Release Requirements:

_____

_____

Entry Date: _____

Assure LLNL requirements are met before and during material transfer. Custodianship is transferred with material. Upon completion of exchange, send message to System Operator.

Figure 3. Explosives Inventory Data Base entry form.

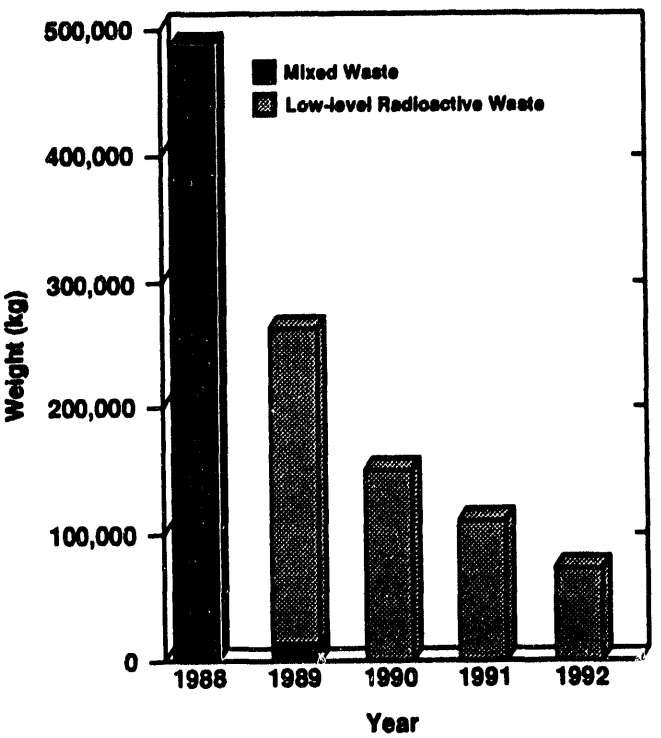

Figure 4. Firing table gravel and debris: waste generated 1988–1992.

FUTURE ACTIVITIES

Plans are underway to examine the feasibility of recycling the gravel component of the wastestream. The gravel component represents approximately 15% of the wastestream. In our new study, we will determine whether it is cost beneficial to sieve, wash, and recycle the gravel and to recycle the water used in the process. This study is planned for late 1993.

ACKNOWLEDGMENTS - Work performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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PRACTICAL UTILIZATION OF MODELING AND SIMULATION IN LABORATORY PROCESS WASTE ASSESSMENTS

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ABSTRACT. At Los Alamos National Laboratory (LANL), facility waste streams tend to be small but highly diverse. Initial characterization of such waste streams is difficult in part due to a lack of tools to assist the waste generators in completing such assessments. A methodology has been developed at LANL to allow process knowledgeable field personnel to develop baseline waste generation assessments and to evaluate potential waste minimization technology. This Process Waste Assessment System (PWAS) is an application constructed within the Process Modelling System. The Process Modelling System is an object-oriented, mass balance-based discrete-event simulation using the Common LISP Object System. Analytical capabilities supported within the PWAS include: complete mass balance specifications, historical characterization of selected waste streams and generation of facility profiles for materials consumption, resource utilization and worker exposure. Anticipated development activities include provisions for a Best Available Technologies. database and integration with the LANL facilities management Geographic Information System The environment used to develop these assessment tools will be discussed in addition to a review of initial implementation results.

INTRODUCTION

The 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) have made the disposal of entire categories of hazardous substances difficult and expensive. Such regulatory imperatives were the consequence of a compelling body of evidence which suggested that historical containment and disposal methods for many such materials had been either inadequate or improper. The resulting wide-spread contamination prompted Congress to mandate minimization of waste production and safe disposal of wastes that cannot be eliminated (1). A successful waste minimization program is dependent on a comprehensive baseline assessment of existing processes and their attendant waste or residue generation. Such baseline assessments may then be used to derive a prioritized list of waste minimization options for each facility or process of interest (2). At Los Alamos National Laboratory, a new class of analytical tools is being developed to assist laboratory waste coordinators and generators in the completion of baseline Process Waste Assessments.

THE PROCESS MODELING SYSTEM

The Process Modeling System (PROMOS) is an object-oriented, discrete-event simulation model developed at Los Alamos National Laboratory. The application has been implemented in the Common LISP pro-

gramming language using the Common Lisp Object System (CLOS) with existing versions available to support a variety of hardware platforms including the Sun Microsystems SPARC, Apple Macintosh and IBM PC architectures. The PROMOS application is fundamentally a system-level simulation tool designed to facilitate the characterization of material flow and transformation in processing facilities of virtually any type.

The simulation model has been employed successfully in a number of highly diverse processing and manufacturing areas. Most recently, PROMOS was utilized in the design phase of project ECOCIRCUIT to characterize all production and waste treatment processes in a printed wiring board (PWB) manufacturing plant prior to actual facility construction. Areas addressed included all chemical, mechanical, and assembly processes anticipated for the new PWB facility. The model has also been applied within the Department of Energy to characterize the processing and waste treatment of transuranic elements in a variety of facilities. Once again, processes for which modeling and simulation undertaken included highly diverse tasks in chemical processing, mechanical assembly, machining activities and foundry operations.

Architecturally, the Process Modeling System has been designed to address two practical aspects of process analysis within a given facility, i.e., material flow and material transformation. Material flow analyses are generally concerned with issues involving overall plant throughput and capacity. PROMOS allows characterization of such material flow as discrete objects, (i.e., parts), batches of material or continuous flows.

In contrast, representation of material transformation is more often associated with individual process lines or locations. Issues of concern include equipment types, quantities and reliability as well as individual process efficiency. Important ancillary issues involve operator procedures and exposures, waste and by-product generation and overall resource availability and consumption. PROMOS supports such characterization of material transformation as discrete objects or variable sized batches.

Material movement and/or material transformation may be modeled with or without constraints.

There currently exists a variety of both general purpose and domain specific simulation tools and environments potentially suited for use in the analysis of processing facilities. The capabilities of PROMOS which differentiate it from other available systems include: (a) range of model detail supported (Fig. 1.), (b) accommodation of worker specific parameters such as exposure levels, and (c) a mass-balance specification methodology which provides a natural mechanism for the modeling of waste generation and residue disposition. In addition, the Process Modeling System possesses a fundamentally open and extensible architecture which facilitates the addition of new capabilities such as product reliability estimation, regulatory compliance information management, and evaluation of alternative technologies.

INFOCAD

InFoCAD is a commercially available Automated Mapping/Facilities Management (AM/FM) system consisting of integrated Computer Aided Design (CAD), Coordinate Geometry (COGO) and Geographic Information System (GIS) modules. InFoCAD was developed by Digital Matrix Services of Miami, Florida, and is currently in use as the facilities engineering repository for Los Alamos National Laboratory.

The logical architecture of the InFoCAD data management facilities (Fig. 2.) consists of two different proprietary database types each composed of several two-dimensional data structures or "tables." The graphical database component of the InFoCAD system consists of five tables: (a) the COGO table for storage of X-Y coordinate information, (b) the Segment table for storage of CAD line segment information, (c) the Figure table for storage of topological (polygonal) data, (d) the Image, and (e) Video tables for maintenance of various image data. The attribute database component of InFoCAD is composed of one or more Domain

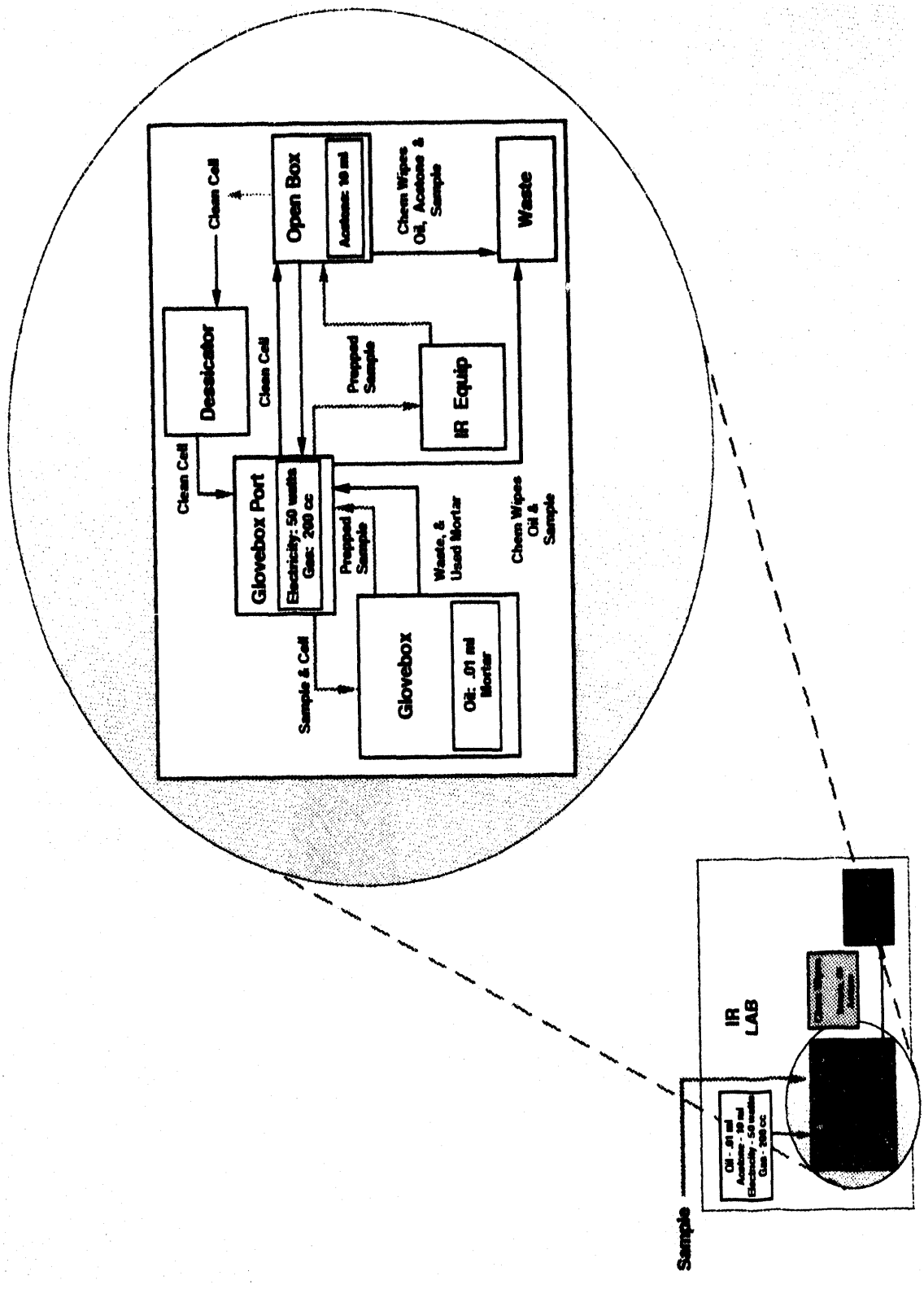


Figure 1. Dynamic Scale of the Process Modeling System

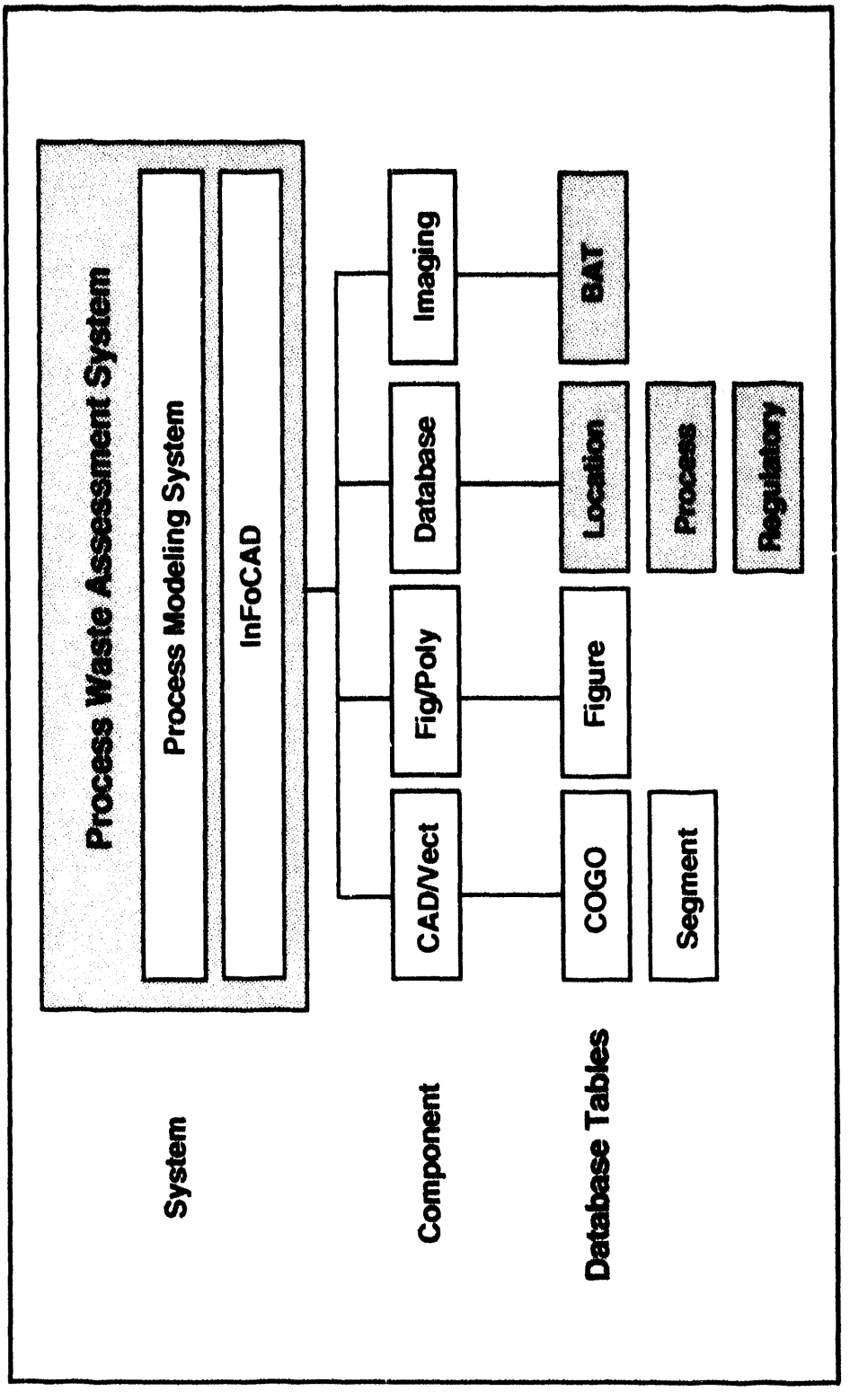
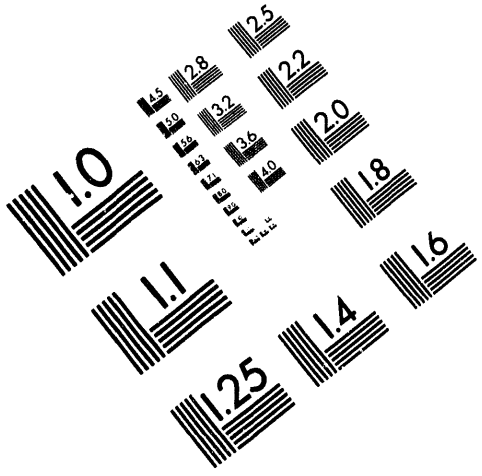


Figure 2. InFoCAD And PWAS Architectures.



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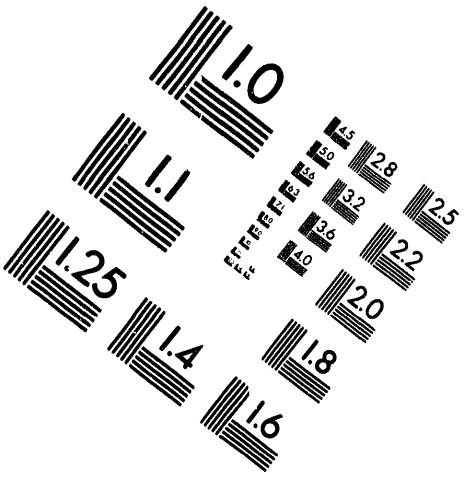

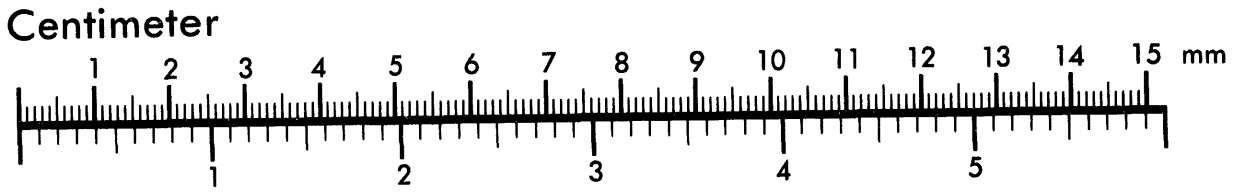

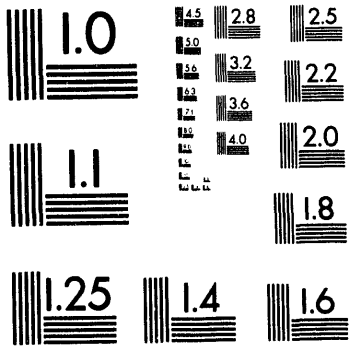

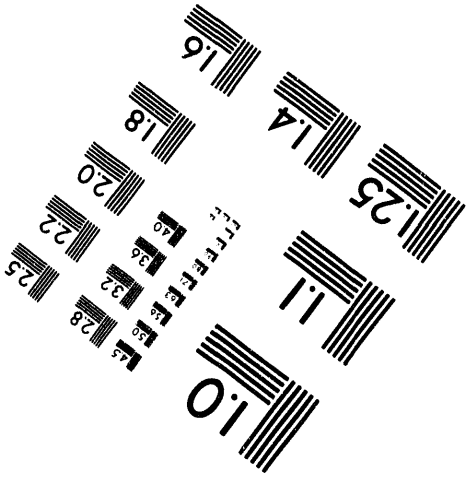

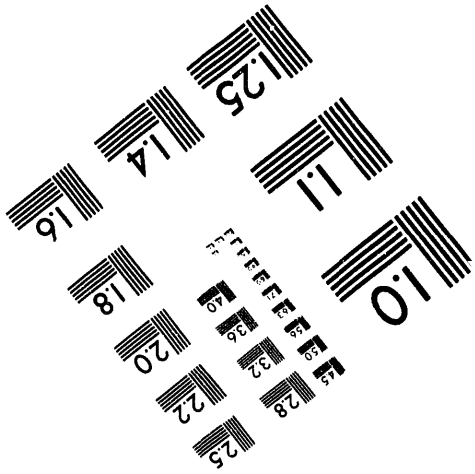

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tables for storage and maintenance of non-graphical or attribute information associated with individual graphical objects.

A novel advantage of GIS products over more conventional database management systems is the ability to support spatial as well as attribute based queries of underlying datasets. This allows a user of the system to select objects of interest based on their location and/or spatial relationship to other objects in conjunction with more orthodox selection via associative queries against attribute information. At Los Alamos, the InFoCAD GIS is being employed as the primary data management system for all engineering related structures within the laboratory campus areas. The scope of facilities mapping currently includes all outfalls, drains, stacks and storage areas within and around existing Laboratory structures. The future inclusion of detailed floor plans for individual structures will ultimately provide a complete framework for the characterization of all waste and residue contributing areas within the Laboratory.

THE PROCESS WASTE ASSESSMENT SYSTEM

In general, the requirements for a comprehensive process waste assessment program are highly specific to each organization. In production environments, the greater regularity of waste/residue type and volume lends itself to waste assessment by a centralized group responsible for facility-wide evaluations. In contrast, Laboratory environments such as those within Los Alamos are more accurately described as diverse collections of individual generating sites each possessing their own characteristic waste types and volumes, each of which may vary significantly over time (3). Under such conditions, external waste assessment audits are far less productive than those performed either by local waste coordinators or the generators themselves. At Los Alamos National Laboratory, local coordinators within each organization are assigned responsibility for storage and disposal of waste and/or residue generated on-site. In addition, these individuals are expected to satisfy waste assessment reporting requirements and develop waste minimization programs for their respective organizations. A historical lack of analytical tools to assist waste coordinators and generators in their assessment tasks has recently been addressed by the development of a Process Waste Assessment System (PWAS). The logical architecture of the PWAS application (Fig. 2.) emphasizes the dual nature of the system. The core of the PWAS architecture is, in fact, a simulation and modeling subsystem implemented using the Process Modeling System described previously. This module is currently implemented as a stand-alone simulation environment whose integration with GIS capabilities is the subject of the following paragraphs.

In addition to meeting the performance requirements for baseline Process Waste Assessments, waste generators and coordinators are routinely tasked with estimating the types and amounts of waste material they will generate in solid, liquid, and gaseous forms. Such estimates are generally required for air and water quality permit applications as well as waste disposal planning. Generators frequently do not possess such information and are therefore unable to provide timely, accurate information on current or projected operations. The use of a simulation-based process assessment tool is expected to enhance the generators' and coordinators' abilities to provide timely, consistent summaries and forecasts of waste generation.

To exercise PWAS, users must first define individual process characteristics and relationships such as input/output mass-balances and material routing. This initial process characterization is currently being accomplished primarily via graphic user interfaces available from within the PROMOS module. Interface enhancements now being implemented would allow the user access to existing location and process specific information via GIS query. Such centralized access is considered particularly crucial to the enforcement of laboratory-wide consistency in naming conventions. In addition, GIS storage of such information affords the user "navigational" access to existing process waste information through use of spatial query facilities. A waste coordinator could, for example, access existing site-specific information by delineating a bounded area or specific site of interest rather than specifying keyword/pattern information to match via an associative query operation. Furthermore, having completed all necessary process definitions, the planned

enhancements to PWAS would allow a user to store the resulting "scenario" in the InFoCAD database rather than in system files as is now the case.

Once all pertinent process specifications have been defined, the process simulation module may be used to perform time-variant analyses of process behavior. Typical output for such analyses include standard reports of materials consumed and product and/or waste generated. The current PWAS architecture exports these results to system files at the conclusion of a simulation run. Enhancements planned for the InFoCAD-integrated version of the system include the ability to store simulation results as site attribute information in the GIS. Such model output would, following validation against historical site information, constitute the baseline waste assessment for the processes of interest. Since the level of detail addressed is often critical to an accurate characterization of process behavior, the user would be provided a mechanism to consolidate PWAS simulation results to provide aggregate views where necessary. At present, this would require manual intervention over several separate simulation exercises with the PROMOS module. Planned system extensions would allow data aggregation within the GIS of previously stored results to provide a dynamic range of view detail. Finally, repetitive simulation exercises with substitution of alternative process technology definitions would provide implicit support for waste minimization related analyses by waste coordinators or generators.

The InFoCAD related modifications necessary to implement the capabilities outlined above are also illustrated in Fig. 2. No fundamental modifications to graphical database components are anticipated. However, additional Domain tables to accommodate process, alternative technology and regulatory permitting information for each site would be required for optional GIS maintenance of such attributes. In addition, future inclusion of image data for Best Available Technology (BAT) data would require implementation of one or more application-specific Imaging tables within InFoCAD.

EXPERIENCE

The Process Waste Assessment methodology using PROMOS has been applied to selected process facilities within Los Alamos to validate the initial system implementation. These trial activities have consistently demonstrated the utility of both the methodology and software in the assessment of diverse processes and waste types. The largest single task undertaken in the pilot tests has been the accurate definition of mass balances for the processes and facilities of interest. Not unexpectedly, the relative complexity of individual processes and their attendant mass balance requirements have proven to be highly variable. More specifically, routine experiments or sampling tests are typically associated with standard Laboratory procedures that specify all material input parameters and output disposal requirements. In contrast, many R&D efforts involve more novel processes whose characteristics are understood in large part only by individual operators or researchers. It is anticipated that the use of a rigorous process assessment tool will assist all waste generators in identifying areas where information is lacking and in defining what data should be collect to correct the deficiency.

SUMMARY

The Los Alamos National Laboratory, is addressing Department of Energy mandated Process Waste Assessment requirements through the development of a new class of analytical tools for waste coordinator and/or generator self-assessment. More specifically, the integration of a system-level process simulation tool with commercial Graphic Information System technology is expected to provide a flexible. Process Waste Assessment tool for the completion of baseline process waste characterization and waste minimization analyses.

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CHAPTER 12

Packaging and Transportation

THE CHALLENGE OF PACKAGING AND TRANSPORTING MIXED WASTE SAMPLES AND RESIDUES ARISING FROM THE DEPARTMENT OF ENERGY'S ANALYTICAL SERVICES PROGRAM

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ABSTRACT. This paper discusses the background and magnitude of challenges that the U.S. Department of Energy (DOE) faces in accomplishing its task to characterize and remediate wastes at its sites. The analytical-sample-shipment needs are discussed, anticipated packaging and transport problems are assessed, and the way in which DOE's Transportation Management Division is preparing to support other DOE organizations in addressing these challenges is summarized. Many challenges arising from the need to ship analytical samples are centered upon resolving packaging issues. Resolution of these challenges will require further efforts to define and quantify packaging requirements better and to develop methods for addressing resultant issues in a timely, an efficient, and a safe manner.

INTRODUCTION

The U.S. Department of Energy (DOE) has created the Office of Environmental Restoration and Waste Management (EM) to address the diverse complex problems associated with the remediation of DOE sites. Included in this office are two companion divisions that are playing vital roles in preparing for and monitoring and implementing the remediation process: the Transportation Management Division [TMD EM-561)] and the Laboratory Management Division [LMD (EM-563)]. One of LMD's goals is "to maximize participation of commercial sector laboratories."(1) Attaining this goal will lead to the need to ship significant quantities of materials from DOE sites to commercial analytical laboratories, and from these commercial laboratories back to DOE sites.

The LMD has proceeded in its efforts and has issued detailed plans for proceeding further. As a result, the packaging and transportation planning by TMD, in support of LMD, has now been able to start in earnest. This LMD planning includes the development of a five year plan (1) and progress toward the scoping of sample needs on a site-by-site basis (2). Thus, at the end of calendar year 1992, LMD and TMD started a cooperative effort to scope out the magnitude of, identify problems with, and better understand and prepare to address the challenges facing DOE in packaging and transporting waste samples and analysis residues (many of which will be mixed wastes) resulting from the environmental and waste characterization sampling activities at DOE sites.

This cooperation between LMD and TMD has included the formation of a Laboratory Sample Packaging

and Transportation Working Group, which includes representatives from TMD, LMD, national laboratories, and DOE support subcontractors. The initial efforts and findings of the working group are provided in this paper, which addresses the challenges faced by DOE to safely and efficiently package and transport mixed wastes in support of laboratory analysis activities.

CHARACTERISTICS OF MATERIALS TO BE SHIPPED

The scoping of the characteristics and quantities of samples needed for analysis and the resulting residues from the analyses is under way. The first estimates for the Idaho National Engineering Laboratory (INEL), have been issued (2). A wide variation is being identified in the types of samples to be obtained, packaged, and transported to analytical laboratories. The INEL study categorized the sample sources as "routine," "waste," and "other" as follows (2):

> *Routine Monitoring.* Samples made to satisfy monitoring requirements for demonstrating compliance to requirements such as those from the Clean Water Act, the Safe Drinking Water Act, and the Clean Air Act. The INEL report indicated that these samples will be typically nonhazardous and nonradioactive.
>
> *Hazardous Waste.* Nonradioactive samples that contain either toxic, corrosive, flammable or reactive chemicals or polychlorinated biphenyls (PCBs) above limits defined by the U.S. Environmental Protection Agency (EPA).
>
> *Radioactive Waste.* Radioactive samples that contain source, special nuclear, or by-product materials. These are further categorized into low-level wastes (LLW), transuranic (TRU) wastes (both contact handled and remote handled), and high-level wastes (HLW).
>
> *Mixed Waste.* Radioactive samples that also contain chemically and/or physically hazardous materials. These are further categorized into mixed LLW, Mixed TRU wastes (both contact handled and remote handled), and mixed HLW.
>
> *Other.* Samples required by remediation that are not covered by the previous categories.

These samples are, of course, uncharacterized and may be either nonhazardous or hazardous. Because of their origin and until they are properly analyzed, conservative approaches generally will be necessary in handling, packaging, and transporting them by the sampling sites. If there is even the slightest potential of hazardous materials in the samples, personnel at the sampling site will need to assume the materials are hazardous and will therefore handle, package and transport them accordingly. The result of this conservative approach will be that many of the samples will be presumed to be of the mixed hazardous category.

In addition to the shipment of samples from the sampling site to an analytical laboratory, there will also be significant transport of materials from the laboratory to storage or disposal sites. Generally, the unused portions of samples, residues from sample analyses, and any secondary waste streams will all need to be returned to the originating DOE site or to some other DOE-designated site for storage or disposal. Because the materials resulting from the sample analyses will be properly characterized, the proper packaging requirements will be readily established for them. It is expected that many of these will be of the mixed waste category. Also, the remaining portion of the samples will have been characterized, and the proper packaging and transportation requirements will be readily established for them.

As has been demonstrated for one DOE site (see the next section of this paper), many of the materials to be shipped are projected to be categorized as mixed waste. This is true whether they are samples being shipped to an analytical laboratory, portions of samples being shipped from an analytical laboratory, or

waste residues arising from the analytical laboratory's activities.

QUANTITIES AND TYPES OF MIXED WASTES AND OTHER MATERIALS TO BE SHIPPED

The estimating of the quantities and characteristics of sample analyses to be requested is under way, and the first estimates for one site, the INEL, have been documented. The evaluation for INEL provides a first perspective of the magnitude of the challenge facing DOE. The report for INEL notes that "the annual number of analytical requests from INEL programs may be biased low."(2) That is, the number of analytical requests will probably be higher than those shown in the report. The following subsections, which summarize the perspective for the INEL site, are derived from Ref. 2; preliminary, unpublished data for the Hanford site; and preliminary, unpublished data for all shipments of TRU wastes, DOE-wide. It is estimated that most of these will be categorized as mixed waste.

Quantities for INEL

Reference 2 documents the number of analytical sample requests, not the number of samples requiring shipment. It is expected that multiple analyses will be made from a single sample. Hence, the number of samples that will be shipped will generally be significantly smaller (possibly, on average, by about a factor of 10) than the number of analytical requests. Regardless of what finally results, the number of potential samples that must be packaged and transported to analytical laboratories is certainly significant, whether the samples are sent to DOE laboratories on the sampling site, to DOE laboratories away from the sampling site, or to commercial laboratories.

The data from the INEL evaluation can be used at this time only as an indicator of the magnitude of the task. The INEL study, which provides projected analytical sample requests per year, over a 10-year period for this one site, are summarized in Table 1.

These data demonstrate that, during the next 10 years, about 1.3 million analytical sample requests can be expected for the INEL site alone. Of these, 83 % will be categorized mixed waste. These mixed waste are expected to be:

21 % mixed LLW,
76 % mixed TRU Waste, and
3 % mixed HLW.

Thus, from these data it can be seen readily that, at least for this one DOE site, the majority of the analytical requests are projected to be categorized as mixed waste and the majority of these mixed waste samples will be mixed TRU wastes.

As noted previously, many analyses may be obtained from a single sample. Also, multiple samples may be shipped in a single package. Considering the need for timely analyses and the need to ship unused portions of samples and secondary waste streams from the analytical laboratories, the shipments involved in the sampling program for INEL alone could approach 100,000 over the next ten years (i.e., about 10,000 shipments per year). This compares with 1992 DOE nation-wide shipping activity of 23,000 shipments of all hazardous materials. Thus, the burden on the DOE packaging and transportation system imposed by sample analysis will be a significant increase over current activities and capabilities.

Table 1. Ten-year summary of projected number of analytical sample requests to be made by INEL (2)

Year	Sample Category						Totals
	Routine Monitoring	Hazardous Waste	Mixed LLW	Mixed TRU Waste	Mixed HLW	Radioactive Waste	
1993	15,482	8,487	20,770	5,487	3,000	1,307	54,533
1994	16,010	6,740	47,243	6,900	3,000	3,556	83,449
1995	14,609	5,586	47,176	10,302	3,135	1,806	82,614
1996	15,219	4,801	27,436	3,985	3,135	806	55,382
1997	15,436	4,585	16,367	51,565	3,135	806	91,894
1998	15,287	6,410	13,795	51,565	3,135	1,306	91,498
1999	15,530	6,184	12,515	51,565	3,135	806	89,735
2000	13,409	7,499	15,144	205,149	3,135	806	245,142
2001	13,652	3,594	12,395	206,749	3,135	806	240,331
2002	10,922	4,999	12,395	205,149	3,135	806	237,406
Grand Totals	145,556	58,885	225,236	798,416	31,080	12,811	1,271,984

Quantities for the Hanford Site

Data were obtained informally for the Hanford site from Westinghouse Hanford Corporation personnel at the first meeting of the Laboratory Sample Packaging and Transportation Working Group. The data show that the number of analytical sample requests (determinations) for the Hanford site will grow from about 1 million in 1993 to 2 million in 1998. The radioactive nature of the samples for these determinations in 1998 is projected to be approximately:

Number of Sample Request (Determinations)	Radioactive Characteristics of the Samples
1,000,000	<10 mrem/h and <100 nCi/g
200,000	10 to 200 mrem/h and <100 nCi/g
350,000	>200 mrem/h
500,000	<100 nCi/g of TRU.

Again, because multiple analyses may be obtained from a single sample and multiple samples may be shipped in a single package, the number of shipments involved in the sampling program for the Hanford site will be significantly less than the number of determinations. Thus, as with INEL, it can be projected that the number of shipments per year for the Hanford site associated with samples and analytical residues arising from analyses could number in the tens of thousands per year.

In addition to the samples required for the remediation of the Hanford site in general, an additional challenge concerns the shipment of core samples from the HLW tanks to analytical laboratories for characterization. These samples will generally require shipment in shielded casks unless the samples continue to be handled under special arrangements, on-site, at Hanford. The core samples are currently transported in 19-in. (0.48 m) segments. A minimum of two full cores are to be taken from each tank. Thus, if future shipping utilizes the 19-in. (0.48 m) core segments, and there are an average of five 19-inch core segments per core sample, a minimum of about 1,770 core segments will require packaging and shipping for the 177 tanks at Hanford. To satisfy tri-party agreements between DOE, the operator of the Hanford site, and the state of Washington, these shipments are projected to occur by 1998. In addition to the core segment shipments, the unused portions of the samples and the analytical residues also will require shipment from the analytical laboratories. In all cases, these shipments will be categorized as mixed wastes.

Quantities of TRU Waste Samples to be Shipped

Based upon preliminary, undocumented data obtained by the working group, the number of required TRU field samples required will grow from about 2300 per year in 1993 (based upon the 5,487 analytical sample requests shown in Table 1, where approximately two analyses are obtained per sample, all from INEL) to more than 20,000 per year beginning in about 2003 (projected to come from the Hanford, INEL, Los Alamos, Oak Ridge, Rocky Flats, and Savannah River sites). Thus, it appears that one of DOE's major challenges will be the shipment of TRU waste samples.

ISSUES AND CHALLENGES IN SHIPPING MIXED WASTES RESULTING FROM SAMPLING ACTIVITIES

At its first meeting, the Laboratory Sample Packaging and Transportation Working Group began to identify a number of challenges and issues that must be addressed if the LMD activities are to proceed efficiently and safely. A significant number of issues were identified, and some of them were viewed as key issues that will need near-term attention by packaging and transportation personnel.

The following lists some of these issues, and discusses them. It was recognized by the working group that varied problems may be faced by different sites in packaging and transporting samples. As other sites are considered, additional issues will arise. High-priority sites for near-term evaluation include the Savannah River, INEL, Rocky Flats, and Los Alamos sites, and the three sites in Oak Ridge.

Need for Efficient Chilled Sample Packages

The EPA imposes a requirement (40 CFR Part 136) (3) upon many samples that, from the time they are obtained until they are tested, they must be maintained at 4°C ($\pm$2°C). This requirement is imposed to allow for the evaluation of the presence of volatiles in the sample.

The samples, many of which could be mixed waste, must therefore be transported in some type of cooled (or chilled) container, and they must be transported rapidly from origin to destination because the low temperature will most likely be maintained using a passive system (e.g., ice). Air transport is therefore required. Currently, no package exists that can be used effectively and efficiently to ship these samples by air; existing packages, which will accommodate ice for a period of days, do not simultaneously satisfy both

the U.S. Department of Transportation (DOT) (4) and International Air Transport Association (IATA) (5) regulations. Thus, a new package design, or perhaps multiple package designs, for chilled samples will be required.

Need for a Standard Policy on Air Shipment of Plutonium

Many mixed waste samples will either be suspected of being, or known to be, contaminated with TRU materials, specifically with plutonium. The current U.S. Nuclear Regulatory Commission (NRC) regulations require that "plutonium in excess of 20 curies per package" must be shipped as a solid and must be packaged in a separate inner container placed within outer packaging that meets special containment requirements (10 CFR Part 71.63) (6). In addition to these requirements, the NRC specifies also that air transport is not allowed unless certain requirements are satisfied (10 CFR Part 71.88) (6). These include either

(a) that the plutonium be contained in a material in which the specific activity is not greater than 2 nCi per gram of material and in which the radioactivity is essentially uniformly distributed; or

(b) that the plutonium be shipped in a single package containing no more than an A_2 quantity of plutonium isotopes (where A_2 is 0.002 Ci for ^{239}Pu and ^{240}Pu, 0.003 Ci for ^{238}Pu, and 0.1 Ci for ^{241}Pu).

Because many samples that require chilling to satisfy EPA requirements will also be plutonium contaminated, air shipments will be required. However, the working group has determined that different sites are interpreting the NRC requirements in different ways. Some sites, apparently based on a conservative interpretation of regulatory requirements, have precluded all air shipments of such samples. A DOE-wide, consistent interpretation of the regulations would resolve this problem.

Need for a New, Diverse Package Design for Shipment of Liquid Samples

The ability of sampling sites to ship multiple samples of mixed wastes in a single package is constrained currently because adequate package designs to accommodate such multiple samples do not exist. The working group has determined that the design of a new package, which could carry large quantities of liquid samples and have the capability of containing either single or multiple bottles and different types of bottles would be useful.

Need to Prepare for Future Enhanced Mixed Waste Shipping Demand

The working group determined that a significant enhancement in the need for packages and shipments of mixed wastes will be needed as the characterization and remediation of DOE sites progress. These needs are driven by many factors. For example, as noted previously, rapid growth in the number of alpha-contaminated, mixed waste samples needing shipment is projected. In addition, as characterization proceeds, more hazardous samples are expected to be obtained. This will require the use of new, enhanced package designs with more shielding or increased capabilities.

In addition, the system must be prepared to accommodate the unexpected. When samples are taken, it may be determined in some cases that the samples may be more hazardous than anticipated. Consequently, packagings must be available to receive these samples. All these factors indicate that there is a need to prepare a "family" of package designs that can accommodate a wide range of mixed wastes.

Need for HLW Sample and Analytical Product Packages

As the number of samples from the HLW tanks at the Hanford site grows, the need to ship samples off-site

to other laboratories can be expected. When this occurs (and it could occur within the next two to three years), there will be a need to

- have available NRC-certified package designs (current certified package designs for shipment of these samples do not exist),
- have NRC-certified package designs for multiple 19-in. (0.48 m) samples (currently, all shipments are made on-site in non-certified package designs, one sample at a time),
- have designed and fabricated more efficient packages for the on-site shipments (this could reduce costs and personnel exposure),
- address package-facility interface issues (current analytical laboratory could not conveniently accommodate certified casks),
- consider upgrading and recertifying existing, commercially available Type B package designs (some commercially available package designs might be adapted to satisfy the HLW-sample shipping requirements), and
- prepare for off-site shipments of unused samples and secondary wastes (if additional analytical laboratories are used, then these materials will require shipment to some location for storage or disposal; certified package designs will be required for these shipments; currently, such shipments are made on-site in uncertified packagings).

Concerning the latter issue, little experience is available in packaging or shipping secondary wastes (generally mixed wastes), waste products from analytical laboratories, and unused samples. The working group has determined that a significant effort may be required to prepare for these activities. As this effort progresses, a number of issues will need to be addressed, including defining where, when and how the mixed wastes arising from analytical laboratory efforts are to be shipped.

CONCLUSION

This paper has elaborated on the LMD program, the magnitude of analytical requests expected from DOE sites, the complexity and magnitude of the packaging and transport problems which are expected to arise, and the manner in which TMD is preparing to support LMD and the DOE sites in addressing these issues. The paper reports on some preliminary efforts by a working group formed by TMD and LMD, that has identified some of the challenging issues that must be addressed if DOE is to accomplish successfully its site characterization and remediation tasks. Many of these challenges are centered upon resolving packaging issues, and these issues have been discussed. Further effort by the working group is expected to better define the challenges, and to result in either defining packaging requirements or to define other methods for resolving the issues in a timely, an efficient, and a safe manner.

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POTENTIAL FOR NATIONAL CONSENSUS STANDARDS FOR THE PACKAGING AND TRANSPORTATION OF MIXED WASTE

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ABSTRACT: The American National Standards Institute (ANSI) has accredited ASC N14 with the scope: "Standards for the packaging and transportation of fissile and radioactive materials, non-nuclear hazardous materials including waste and mixed materials, but not including movement or handling during processing and manufacturing operations." The Secretariat for N14 is the Institute of Nuclear Materials Management. N14 has seven standards approved by ANSI and four additional standards are being developed. All of these are focused on radioactive, non-hazardous materials and activities. The infrastructure and processes exist for the development and coordination of American National Standards for mixed waste packaging and transportation. N14 includes an existing scope review committee for proposed N14 Hazardous Materials Standards. N14 could readily respond to any suggested need for mixed waste standards, within the approved scope. Such potential standards might parallel present N14 standards and activities. N14 is organized to expedite the development of consensus standards within its approved scope, to support urgent programs of national interest.

N14 STANDARDS DEVELOPMENT

The American National Standard Institute (ANSI) has accredited N14 Packaging and Transportation of Radioactive and Non-Nuclear Hazardous Materials as a standards developing committee. The Secretariat for N14 is the Institute of Nuclear Materials Management (INMM). The current approved scope of N14 is "Standards for the packaging and transportation of fissile and radioactive materials, non nuclear hazardous materials including waste and mixed materials, but not including movement or handling during processing and manufacturing operations." Standards are developed and maintained in accordance with American National Standards Institute *Procedures for the Development and Coordination of American National Standards*, September 9, 1987 (1) . Specific procedures used by N14 and approved by ANSI are "Model Procedures for an Accredited Standards Committee - Appendix A" (2) which are part of the above document, Ref. 3. Additional procedures used by N14 are in the N14 Procedures Manual.

The N14 committee is guided by a management committee of about 12 members including the Chair and Secretary. There are currently 80 voting members including seven alternates who represent a number of government agencies involved in either the transport or packaging of radioactive and non-nuclear hazardous materials including mixed wastes, vendors of related equipment, shippers, carriers, regulators, utilities, and other interested organizations and individuals. In addition, there are approximately 125 individuals serving on the various Writing Groups which are responsible for preparing standards for N14 balloting and subsequent ANSI approval and maintenance of the standards after they are approved.

We are also seeking to expand the N-14 Committee to include individuals or representatives of organizations from the disciplines of Waste Management, Environmental Control, and Industrial Hygiene and from the Chemical Industry. Anyone interested in becoming a member of the N14 committee should contact the N14 chair.

The N14 membership currently includes eight Ph.D's (technical degrees), three with advanced degrees, and 16 professional engineers that are licensed in at least one state. A tabulation of the disciplines is as follows:

Discipline	Number
Mechanical Engineer	18
Chemical Engineer	9
Physics	10
Nuclear Engineer	5
Ceramic Engineer	1
Civil Engineer	1
Electrical Engineer	2
Metallurgical Engineer	1
Chemistry	3
Business Administration	3
Law/Insurance	2
Law Enforcement	2
Heath and Environmental Control	5
Transportation Management	8
Regulatory	6
Engineer	4
Total	80

N14 complies with the requirement for completion of ANSI Project Initiation Notification System Input Form and the Nuclear Standards Board *Supplement for All New Projects.*

N14 has seven standards approved by ANSI and is in the process of developing four other standards.

The standards that have been approved are:

ANSI N14.1-1990	Packaging of Uranium Hexafluoride for Transport
ANSI N14.5-1987	Leakage Tests on Packages for Shipment of Radioactive Materials
ANSI N14.6-1993	Special Lifting Devices for Shipping Containers Weighing 10,000 Pounds (4500 kg) or More for Nuclear Materials
ANSI N14.19-1986	Ancillary Features of Irradiated Shipping Casks
ANSI N14.24-1993	Barge Transport of Radioactive Materials
ANSI N14.27-1993	Carrier and Shipper Responsibilities and Emergency Response Procedures for Highway Transportation Accidents involving Truckload Quantities of Radioactive Materials

ANSI N14.30-1992 Semi-Trailers Employed in the Highway Transport of Weight-Concentrated Radioactive Loads - Design, Fabrication, and Maintenance

The four standards being developed are:

N14.2 Tiedowns for truck transport of radioactive materials

N14.7 Guide to the Design and Use of Shipping Packages for Type A Quantities of Radioactive Materials

N14.23 Design Basis for Resistance to Shock and Vibration of Radioactive Materials Packages Greater Than One-Ton in Truck Transport

N14.26 Guidance on Quality Control Activities as They Relate to the Inspection, Preventive Maintenance, and Post-Incident Testing of Packages for Shipment of Radioactive Materials

There are two other projects that are being developed:

N14.10 Guide for Liability and Property Insurance Aspects in Shipping Nuclear Materials

N14.25 Tiedowns for Rail Transport of Fissile and Radioactive Material

Several other potential projects are being considered, one on industrial packages, one on training regulations, and one on development of a numerical model for thermal evaluation of UF_6 cylinders. In addition, a planning guide for light-water reactor spent fuel transportation is in progress. This planning guide will not be part of the standards process but will be a replacement for ASTM-E-846, established by the American Socity for Testing Materials (ASTM), which was withdrawn and N14 has accepted responsibility.

In May 1985, a N14 Ad-Hoc Committee undertook a project to study the need for voluntary standards pertaining to spent nuclear fuel and high level waste packaging. As a result of this study, it was determined that a method of identifying and developing needed standards should be created. In order to accomplish this, a N14 Peer Review Panel concept was developed and a charter was prepared. The Charter states (3) that the N14 Peer Review will: (1) provide independent review and commentary on important specifications and documents dealing with the packaging and transportation of nuclear materials, as directed by the N14 Management committee. Such review will be timely, responsive, and well-balanced. Both industry and public interest will be fully represented; (2) establish a mechanism to expedite the development of consensus standards to support urgent programs of national interest; and (3) establish a formal mechanism for industry and public interest sectors to effectively cooperate with Federal agencies on the content of controlling standards and specifications governing national programs. This initial Charter has been prepared for the review of U.S. Department of Energy documents. This Charter can be modified, if appropriate, for documents of other Federal agencies and industry.

POTENTIAL FOR NATIONAL CONSENSUS STANDARDS

N14 has the organization and procedures to effectively develop, coordinate and process standards for non-nuclear, hazardous materials and mixed wastes. N14 is not actively seeking out areas where standards should be written, but rather much prefers to have potential projects or documents brought to it for standards consideration. N14 has established a scope review committee (4) which will review and evaluate proposed scopes and make a recommendation prior to initiating the project.

N14 will address packaging issues as they relate to the hazard of materials and their attendant risk during transportation. Areas that may need standards consideration are: (1) HM-181 packaging certification and performance criteria, (2) mixed waste containers and their transportation, and (3) Resource Conservation and Recovery Act/Hazardous material storage packaging and labelling. The need to control costs, reduce scrap, improve safety, improve production, and maintain or improve quality are additional broad areas for standards consideration.

Potential standards consideration could parallel some of the existing N-14 standards and activities for radioactive materials which include:

- Inspection procedures including leakage tests on packages
- Special handling and auxiliary equipment features including design ,fabrication, and maintenance
- Guides for operating manuals for packaging
- Emergency response procedures
- Guides for liability and insurance aspects

In summary, N14 is the ANSI accredited standards organization to develop packaging and transport consensus standards within its approved scope. If standards are needed, we would welcome your suggestions and support from your experts to serve on Writing Groups. We would also welcome interested experts to join our N14 Committee.

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TRANSPORTATION OF LIQUID MIXED WASTE IN THE U.S.: IS IT REALLY A PROBLEM?

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ABSTRACT. The transportation of liquid radioactive wastes has often been perceived to be a problem because of the potential consequences from hypothetical accident scenarios and the difficulties that may be encountered in the handling and containment of liquids. This paper focuses specifically on liquid mixed waste and examines the current U.S. regulations that govern their transportation to determine if the transportation of these wastes are severely restricted by the regulations. The paper also compares current practices for the transportation of liquid mixed waste in the U.S. with that of France to provide an international perspective on the issue. The review of the regulations and current practices shows that the transportation of liquid mixed waste is by no means prohibited, and also that the majority of the regulations do not impose any additional restrictions because of the physical form of the waste. Rather, the selection of an authorized package primarily depends on the quantity of radioactivity and the specific radionuclides involved. Although the selection process for an authorized package for liquid mixed waste is fairly straightforward, it seems that the difficulties in transporting liquid mixed waste can be attributed to the lack of readily available Type A packages designed for transporting liquids.

INTRODUCTION

The packaging and transportation of radioactive mixed wastes have often raised significant concerns to transporters because of the multiple set of regulations governing mixed waste. Since mixed waste is comprised of a radioactive component and a hazardous waste component, the regulatory requirements for its transportation appear in the following three separate codes of federal regulations; regulations mandated by the U.S. Nuclear Regulatory Commission (NRC) to address the transportation of radioactive waste (1); regulations promulgated in accordance with the Resource Conservation and Recovery Act (RCRA) that authorize the U.S. Environmental Protection Agency (EPA) to regulate the transportation of hazardous waste as codified in 40 CFR 262 and 40 CFR 263 (2,3); and the regulations mandated by the U.S. Department of Transportation (DOT) in 49 CFR 171 through 178 to address both radioactive and/or hazardous waste shipments (4). These regulations do not address mixed waste as a unique waste, and therefore, both the hazardous and radioactive properties of the waste must be evaluated in order to determine the applicable regulations governing its transportation.

The unique procedures associated with the packaging and transportation of mixed waste, in general, have been discussed earlier by McCall and Calihan (5). Public perception and other issues and challenges associated with the packaging and transportation of radioactive waste in general have also been discussed previously by many authors (6-10). This paper focuses specifically on the transportation of liquid mixed waste. Transporting liquid radioactive waste has often been perceived to be a problem because of the potential consequences from hypothetical accident scenarios and also due to the difficulties that are encountered in the handling and containment of dispersible substances such as liquids. This paper examines whether the packaging and transportation of liquid mixed waste is a problem that can be

attributed to the stringency of the regulations, or if liquid waste transportation is simply perceived to be more difficult than it is in reality. Specifically, this paper discusses current U.S. regulations for packaging and transporting mixed waste with a special emphasis on any restrictions that are applicable only to liquid waste. It also compares current practices for transporting liquid mixed waste in the U.S. with the current practices for transporting radioactive liquids in France to provide an international perspective on the issue. Finally, the paper examines the availability of appropriate packages and presents the summary and conclusions regarding the various issues that influence the transportation of liquid mixed waste in the U.S.

U.S. REGULATIONS FOR PACKAGING AND TRANSPORTATION OF LIQUID MIXED WASTE

As mentioned previously, the packaging and transportation of mixed wastes in the U.S. is governed by three sets of federal regulations, which are administered by the EPA, the NRC, and the DOT. The following sections summarize the salient points of each set of regulations, especially with respect to liquid mixed waste. For the purpose of transportation, the term radioactive material is defined by DOT in 49 CFR 173.403 as any material having a specific activity greater than 0.002 μCI/g (4). Also, this paper assumes the DOT definition of 'liquid' in 49 CFR 171.8, which defines liquid as a material that has a vertical flow of over 2 in within a three minute period when determined in accordance with procedures specified by certain ASTM standards (4).

RCRA Regulations for the Transportation of Hazardous Wastes

The emphasis of RCRA with respect to waste transportation is primarily on proper characterization of the waste prior to transportation. The generators of hazardous waste are delegated pre-transportation responsibilities under 40 CFR 262, "Standards Applicable to Generators of Hazardous Waste" (2). Generators are solely responsible for characterizing their waste, either by analytical testing or by "applying knowledge of the hazardous characteristics of the waste in light of the materials or the processes used." Also, under 40 CFR 264.13, RCRA regulations require that an owner/operator of a treatment, storage, or disposal facility obtain a detailed chemical and physical analysis of "a representative sample" of the waste before undertaking any treatment, storage, or disposal activity (11). In general, because of the homogeneous nature of liquids, collecting a "representative" sample from a container of liquid mixed waste may not pose a problem provided that effective precautions are taken to prevent any harmful exposure to radioactivity. Thus, in comparison with heterogeneous solid waste forms, it may actually be easier to characterize liquid mixed waste by analysis of a "representative" sample. While the characterization activities do not directly address the regulations regarding packaging and transportation of liquid mixed waste, they do influence the ability of a waste generator to prepare the liquid waste for shipment.

Transporters of hazardous waste are also subject to the guidelines defined in 40 CFR 263, which essentially require transporters to comply with the manifest system. Subsequent to waste characterization and prior to shipment, RCRA requires a waste generator to prepare a manifest, otherwise identified as a "Uniform Hazardous Waste Manifest". In order to prepare such a manifest, some of the items the generator must know are the DOT hazard class, proper shipping name, and the quantity of the waste. In addition, some states might require waste specific information such as concentration and RCRA codes for hazardous constituents. Such determinations may be made either through knowledge of the waste generation process or by sampling and analysis. As mentioned earlier, the homogeneous nature of most liquid wastes is likely to make them relatively easy to characterize and prepare manifests.

With respect to the actual packaging requirements, RCRA requires that the EPA's regulations be consistent with the DOT regulations under the Hazardous Materials Transportation Act (HMTA). Therefore, in 40 CFR 263.10, the EPA has specifically incorporated the DOT regulations (3). This

assures consistency between the EPA and the DOT regulations. The specific DOT requirements for labeling, marking, and placarding for liquid mixed waste are the same as those that apply to other hazardous materials except that the packaging requirements also depend upon the level and type of radioactivity present in the waste. The DOT regulations are discussed in a subsequent section.

NRC Regulations for the Transportation of Radioactive Waste

The NRC has responsibility for safety in the transport of radioactive waste, as stipulated by the Atomic Energy Act. Since both the DOT and the NRC have statutory authority to regulate the transportation of radioactive materials, including wastes, it was necessary for an agreement to be reached that delineated the responsibilities of each agency, to avoid conflicting and redundant standards. This agreement was outlined in a Memorandum of Understanding between the two agencies for regulation of safety in the transportation of radioactive materials (12). The NRC outlines exemptions for low level materials in 10 CFR 71.10 (1). Any package containing radioactive material having a specific activity not greater than 0.002 μCi/g is exempt from all requirements of 10 CFR 71, including the section that requires compliance with DOT regulations. In addition, packages that contain a quantity of radioactive material that is either equal to or less than the amount allowed by the DOT in Type A packages, and an allowable amount of fissile material (exempted by 10 CFR 71.53), are also exempt from all requirements of 10 CFR 71 except the section that requires compliance with DOT regulations.

The primary emphasis of 10 CFR 71 is on the proper packaging of radioactive materials and the allowable contents of a package. In this case, allowable contents are determined by the activity of the waste, not the physical form. The general standards for all packages to be utilized for radioactive material transport are presented in 10 CFR 71.43. The most important of these standards which could affect the packaging of liquid mixed waste are: the elimination of reaction potential between container and contents; the requirement for the package to have a device for containment of any leakage (vapor or liquid) from the container; and the requirement for the package to be designed, constructed, and prepared for shipment so that it operates effectively under normal transportation conditions. Tests to simulate normal transportation conditions (defined in 10 CFR 71.71) include water spray, free drop, corner drop, compression, and penetration tests. Type B packages must satisfy the additional requirements of 10 CFR 71.51 which include hypothetical accident condition tests defined in 10 CFR 71.73. These standards include more stringent conditions for the free drop test, as well as puncture, thermal, and immersion tests.

Liquid radioactive materials are specifically addressed by 10 CFR 71.87 which requires that the licensee ensure that the package with its contents satisfies the requirements of the license for the package. In addition, the licensee shall determine that any system for containment of liquid is adequately sealed and has adequate space or other specified provision for expansion of the liquid.

DOT Regulations for the Transportation of Liquid Mixed Waste

The DOT has regulatory responsibility for the transportation of hazardous materials by all modes and means of interstate transportation. It should be noted that in the DOT regulations (49 CFR 171.8) the term "hazardous materials" is used (2) to refer to a wide variety of materials and is not limited to its usual connotation under RCRA (4). Of the three sets of federal regulations governing the transportation of mixed waste, the DOT regulations (49 CFR 171-178) are the most extensive in determining the appropriate package for any waste material, including liquid mixed waste.

As discussed earlier, the DOT assigns hazard classes and divisions that govern the packaging, labeling, marking, and shipping paper requirements of hazardous materials. The hazard classes and divisions for different materials are shown in the Hazardous Materials Table in 49 CFR 172.101. The classification of a material having more than one hazard (e.g., liquid mixed waste which could potentially exhibit

corrosivity in addition to being radioactive and hazardous) is determined from the hierarchy defined in 49 CFR 173.2a. Radioactive materials are assigned a hazard class of 'Class 7', which has the highest priority. Liquid waste forms do not require any special hazard class designation. The DOT regulations for labeling and marking of hazardous waste are described in 49 CFR 172. Since the most significant component of radioactive waste transportation is the packaging of the waste, the discussion in this section is limited to the steps involved in the selection of an appropriate package for liquid mixed waste that will meet DOT requirements.

The DOT requirements for proper packaging of all hazardous materials, including liquid mixed waste, is outlined in 49 CFR 173. The specific packaging requirements for liquid mixed waste depend on many parameters. The major parameters are the form of the radioactive material ('special' or 'normal' form as defined by 49 CFR 173.403), and the quantity of radioactivity and specific radionuclides being transported. A discussion of each of these parameters and how they affect the transportation of liquid mixed waste is presented below.

Form of radioactive material. The DOT regulations (4) classify radioactive material into 'special form' and 'normal form' (4). Radioactive materials need to satisfy three different requirements to qualify as special form. The most stringent of these requirements is that the material must either be a single solid piece or must be contained in a sealed capsule that can be opened only by destroying the capsule. Any radioactive material which does not qualify as special form is classified as normal form. Since special form materials are less likely to disperse in the event of a packaging failure, the DOT regulations allow substantially larger amounts of these materials per package relative to normal form materials. Due to the considerable cost of sealing high volumes of liquid mixed waste in a capsule, it is expected that in general most liquid mixed waste will be classified as normal form.

Quantity of radioactivity. The DOT has established two parameters, A_1 and A_2, which dictate the packaging requirements for all radioactive materials including liquid mixed waste. A_1 and A_2 are the maximum activities of special form and normal form radioactive material, respectively, that are permitted in a Type A package (4). The values of A_1 and A_2 for single radionuclides are listed in 49 CFR 173.435 and have a limiting A_2 value of 0.002 Ci for some transuranic radionuclides such as plutonium. In general, the value of A_1 for a given radionuclide is higher than A_2 indicating that greater amounts of radioactivity are allowed per package if the material qualifies as special form. In cases where the material being transported contains a mixture of radionuclides, the values of A_1 and A_2 are determined according to procedures outlined in 49 CFR 173.433(b). Most liquid mixed waste is anticipated to fall in this category. For mixed fission products where a detailed analysis is not carried out, A_1 and A_2 have values of 10 Ci and 0.4 Ci, respectively. 49 CFR 173.433(b) also includes detailed procedures for determining activity limits and verifying Type A package eligibility for single radioactive decay chains, mixtures where identities and activities of each radionuclide are known, and also for cases where the mixture is not adequately characterized for radionuclide content. The most restrictive limits apply when the identity of radionuclides is not known. These limiting values of A_1 and A_2 are 2 Ci and 0.002 Ci, respectively. However, if alpha emitters are known to be absent, the value of A_2 is increased to 0.4 Ci. Any radioactive material that exceeds the A_1 and A_2 values as determined by 49 CFR 173.433 and 49 CFR 173.435 is required to be transported in a Type B package.

The general design requirements for Type A packages are listed in 49 CFR 173.411 and 173.465, while the requirements for Type B packages are listed in 10 CFR 71. By DOT definition, the primary difference between the two types is that while Type A packages are designed to retain the integrity of containment and shielding during normal conditions of transport only, a Type B package is designed to withstand hypothetical accident conditions as well (4).

The values of A_1 and A_2 are solely dependent on the radionuclide composition of the material being

transported and are not dictated by its physical form. Thus, these values are the same irrespective of the waste being in solid or liquid form. However, the DOT does impose additional restrictions on Type A packages if they are used for transporting liquids and prohibits the transportation of pyrophoric radioactive materials in liquid form (4). These restrictions are documented in 49 CFR 173.412(n) and 49 CFR 173.466. As per 49 CFR 173.412(n), a Type A package designed for a liquid volume exceeding 50 cm^3 must either have sufficient absorbent material to absorb twice the volume of the liquid contents, or it must have inner and outer containment systems designed to assure retention of the liquid contents in case of a leak. 49 CFR 173.466 imposes additional restrictions on the mechanical strength of Type A packages designed for liquids and gases. These restrictions increase the distance of fall in both the "free drop test" and the "penetration test" described in 49 CFR 173.465 for normal Type A packages. For Type A packages designed for liquids, this distance is increased from 1.2 m to 9 m for the 'free drop test' and from 1 m to 1.7 m for the 'penetration test'. Since these are substantial increases, it can be concluded that the DOT regulations are much more restrictive regarding the use of Type A packages for transportation of liquid mixed waste as compared to shipment of solid waste using Type A packages.

The DOT does have provisions for two special cases where the transportation of liquid mixed waste can potentially qualify for less restrictive regulations than described above. These two special cases are categorized as "limited quantity of radioactive material" (4) and "low specific activity" (LSA) material (4).

Materials that qualify as "limited quantity of radioactive material" are exempted from all DOT requirements associated with packaging including package specifications, shipping paper and certification, marking, and labeling. The primary requirement for all liquids (other than tritiated water) to qualify as "limited quantity of radioactive material" is that the total activity in the package must not exceed 10^{-4} times the value of A_2. If the package contains only tritiated water, the maximum allowable activity could vary between 1 to 1,000 Ci depending upon the concentration in Ci/L. The other significant requirement for qualifying as limited quantity is that the radiation level at any point on the external surface of the package cannot exceed 0.5 mrem/hr. If a given liquid mixed waste qualifies as a limited quantity of radioactive material it can be transported in strong tight packages that will not leak any of the radioactive materials during normal conditions of transport. In comparison to liquid radioactive waste, the activity limit for a package of solid radioactive waste to qualify as limited quantity material (10^{-3} times the value of A_2) is an order of magnitude higher, which shows that even in this case the DOT regulations are more restrictive for liquids.

Liquid mixed waste can qualify as LSA material if it satisfies any one of the five criteria listed in 49 CFR 173.403. Of these five criteria there are two which are relevant to liquids. Liquid mixed waste containing tritium oxide in aqueous solutions can qualify if the concentration does not exceed 5 mCi/mL. Also, material in which the radioactivity is uniformly distributed (such as liquid mixed waste) can qualify as LSA if the average activity does not exceed 0.0001 to 0.3 mCi/g depending upon the A_2 value for the particular radionuclide. As an example, liquid mixed waste containing only plutonium-239 (for which A_2 = 0.002 Ci) would qualify as LSA if the average concentration does not exceed 0.0001 mCi/g, provided that the total activity in the package does not exceed the value of A_2=0.002 Ci which is the limit for plutonium-239 in a Type A package. This implies that in order to simultaneously qualify as LSA material and also meet the A_2 limit for plutonium-239, the volume of aqueous liquid waste transported in a package cannot exceed 20 L. Liquid mixed waste qualifying as LSA material can be transported in one of two ways (4). For non-exclusive use shipments, a Type A package is necessary. However, the additional restrictions on liquid transport imposed by 49 CFR 173.412(n) and 49 CFR 173.466 regarding the mechanical strength of the package and the use of absorbents do not apply to LSA materials. For exclusive use shipments, LSA materials are exempted from many DOT requirements. These exemptions are similar to the ones described earlier for limited quantity radioactive materials except that the allowable radiation levels at any point on the external surface of the package are significantly higher for LSA materials. Also, for exclusive use shipments, liquid mixed waste qualifying

as LSA material can be transported in bulk in tank cars that satisfy DOT specifications listed in 49 CFR 173.425.

COMPARISON OF LIQUID WASTE SHIPMENT PRACTICES IN THE U.S. AND FRANCE

The status of current practices for transportation of liquid mixed waste in the U.S. was studied by collecting information from a few select companies that receive shipments of liquid mixed waste for subsequent treatment. In addition, information available on the transportation of radioactive liquids in France was studied in comparison to current U.S. practices.

Three U.S. companies were identified that receive liquid mixed waste shipments for treatment. Diversified Scientific Services, Incorporated (DSSI) in Kingston, Tennessee, can receive liquid radioactive waste in containers ranging from 5 to 85 gallon drums as well as in tanker trucks (13). Almost all of the liquid mixed waste received by DSSI qualifies as LSA material and therefore no major problems are encountered in the transportation process (14). Nuclear Source Services, Incorporated (NSSI) in Houston, Texas, has various existing and planned treatment units to handle liquid mixed waste. The majority of the liquid mixed waste which they receive is LSA and therefore exempt from the most stringent DOT and NRC regulations (15). However, they do receive some Type A packages of liquid mixed waste, as defined by the shipper. One of these Type A packages is comprised of a 55-gallon drum overpack, which includes a liquid container with a capacity of 16 gallons or less that acts as a primary inner containment vessel and is surrounded by adequate absorbent material (usually vermiculite) to meet the restrictions imposed by 49 CFR 173.412(n) (15). Quadrex Environmental Company in Gainesville, Florida, receives scintillation vials from various government and commercial clients. Essentially all the shipments received by Quadrex contain liquid mixed waste that can qualify as LSA material (16).

Apart from the above commercial facilities, some U.S. Department of Energy (DOE) sites such as the Feed Materials Production Center in Fernald, Ohio, the Portsmouth Gas Diffusion Plant in Portsmouth, Ohio, and the Paducah Gas Diffusion Plant in Paducah, Kentucky, have all shipped liquid mixed waste to the DOE Oak Ridge Reservation for treatment in the TSCA Incinerator facility (17,18). Since these wastes qualified as LSA material they were all shipped in bulk using tanker trucks.

The experience acquired at the Saclay Nuclear Research Center in France in the transport of liquid radioactive wastes has contributed to the development of three tank trailer models for radioactive liquid transportation (19). These trailers have been approved by the French Ministry of Transport and used frequently for transportation in France and also in other European countries. The three different trailers, which are all equipped with a tank and range in capacities from 1.28 m^3 to 4.5 m^3, are designed for low-level, intermediate level, and high-level liquids. The trailer for the low-level liquids has a radioactivity limit of 100 times A_2, which is higher than the U.S. limit for a Type A package and much higher than the limits for liquids qualifying as LSA materials that can be transported in bulk. The trailers for intermediate and high level liquids are Type B packages and have radioactivity limits of 3,000 times A_2 or 30,000 curies, whichever is less. These radioactivity limits are identical to the 'highway route controlled quantities' defined in 49 CFR 173.403 (4). While the regulations governing the transport of intermediate level and high level liquids seem similar between the U.S. and France, the U.S. regulations for the transport of low level liquids seem to be more restrictive than their French counterparts.

PACKAGES AVAILABLE IN THE U.S. FOR TRANSPORTATION OF LIQUID MIXED WASTE

The Radioactive Materials Packaging (RAMPAC) database was used to identify Type A and Type B packages that are available for the transportation of liquid mixed waste (20). The RAMPAC database, which is maintained by Analysas Corporation in Oak Ridge, Tennessee, is designed to store and retrieve

information on all non-classified packagings certified by the NRC, the DOE, and the DOT for transportation of radioactive materials within the U.S. It is a useful tool available to transporters of radioactive material that contains and reports packaging information from all three federal agencies. RAMPAC contains information on over 650 radioactive material shipping packagings. Examples of the types of information for each packaging that may be stored in RAMPAC include weights (gross, payload, empty), measurements, agencies authorizing its use, shielding and coolants used, authorized contents, and organizations authorized to use the packaging. A preliminary search of the RAMPAC database has indicated that there are no Type A containers currently available that are designed to handle liquids. Three Type B containers were identified by the database that are certified to handle the transportation of liquid mixed waste.

SUMMARY AND CONCLUSION

The three sets of U.S. federal regulations mandated by the EPA, the NRC, and the DOT, that govern the transportation of hazardous and/or radioactive materials were reviewed to determine the stringency of these regulations towards the transportation of liquid mixed waste. The review shows that the transportation of liquid mixed waste is not prohibited by any regulation irrespective of radioactivity levels, except for radioactive pyrophorics which are prohibited from transportation in liquid form. In general, the package selection process for transportation of liquid mixed waste seems to be dictated by the specific radionuclides and their total activities per package rather than the concentration of the RCRA-hazardous constituent present in the waste.

The portion of the RCRA regulations that regulates transportation (2,3,4) focuses primarily on waste characterization prior to transportation, and does not seem restrictive with respect to the transportation of liquid mixed waste. In fact, in comparison to heterogeneous solid wastes, it may actually be easier to characterize and transport liquid mixed wastes because of their homogeneous nature as long as all DOT requirements are met with respect to packaging. Likewise, the NRC regulations (1) also do not impose any significant additional restrictions with respect to the transportation of liquid mixed wastes because of their physical form. The NRC regulations focus on tests for Type B containers under hypothetical accident conditions. The main hindrance to transporting liquid mixed waste seems to be the limited number of certified packages that are available to transport liquid mixed waste containing radioactivity in excess of the levels permitted in a Type A package.

The DOT regulations are more restrictive for liquid mixed waste in comparison to solid waste if the waste is transported in a Type A package. However, if the liquid mixed waste can be adequately characterized to show that the levels of radioactivity are low and the waste does qualify either as limited quantity material or as LSA material, the restrictions from the DOT regulations are significantly reduced. Liquid mixed waste qualifying either as limited quantity or as LSA material has no additional constraints transportation in comparison to solid waste. On the contrary, since the criteria for LSA material emphasizes the uniform distribution of radionuclides, liquids may actually have a better chance of qualifying as LSA material because of their generally homogeneous nature.

A brief comparison between current practices for transporting radioactive liquids in the U.S. and similar practices in France indicates that the U.S. regulations have lower activity limits per package for low-level liquid waste. Therefore, the U.S. regulations are more stringent for the transportation of low-level radioactive liquid waste. Although the activity limits per package for intermediate and high-level liquid waste are similar between the U.S. and France, the data show that the quantity of liquid waste that has been transported in France far exceeds the quantity transported within the U.S.

In summary, in spite of the multiple sets of regulations governing the transportation of liquid mixed waste, the procedures for the determination of an appropriate package are fairly straightforward especially

if the waste has been subjected to adequate radiological characterization. If the waste is not adequately characterized, it can still be transported but it will require the selection of the package to be based on conservative assumptions. This can substantially decrease the amount of waste per package and thereby increase the number of shipments. Therefore, it is in the interest of the transporter to adequately characterize the waste prior to shipment. It can be concluded that the packaging and transportation of liquid mixed waste is well defined under the existing U.S. regulations. However, it seems that the real problem is not the stringency of the regulations but the lack of availability of suitable Type A containers for waste that does not qualify as either limited quantity or LSA material and also does not exceed the A_2 value for Type A packages.

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TRANSPORTATION OF DOE MIXED WASTE IN THE U.S.

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ABSTRACT. Mixed low-level waste (MLLW) is stored at various U.S. Department of Energy (DOE) sites across the country. This waste includes liquids, contaminated solids, and a host of hazardous materials with radioactive contamination. A question of great institutional interest is the number and location of treatment facilities. Centralization or regionalization of facilities is being considered because of economies of scale. Either centralized or regionalized facilities will require the transportation of large quantities of waste. This paper explores a variety of issues affecting the location and number of treatment facilities. These issues include the relative distribution of MLLW at different DOE locations, the regulatory framework governing the transportation of untreated MLLW, activities that may be required to prepare the waste for transportation, and the uncertainties of public and state acceptance of transportation of MLLW through state boundaries. Finally, based on the analysis of these issues, the paper summarizes the relative merits of centralized versus decentralized schemes with respect to waste transportation.

INTRODUCTION

Mixed low-level waste (MLLW) has been generated and continues to be generated at more than 30 DOE sites across the U.S. A substantial amount of this waste is subject to the Land Disposal Restrictions (LDR) (1), and must be treated to satisfy LDR standards prior to disposal. Although economies of scale are expected to result from the regionalization or centralization of treatment facilities, either of these options would incur the cost of transporting large amounts of untreated MLLW. Thus, there is an obvious trade-off involved between consolidation of treatment facilities versus transportation costs. The different issues that should be considered for selecting the appropriate number and location of treatment facilities are a subject of considerable debate. This paper summarizes various transportation issues that need resolution prior to treatment facility siting, and explains how each issue may influence the selection of the number and location of MLLW treatment facilities. Specifically, the paper discusses the relative distribution of different types of MLLW at U.S. Department of Energy (DOE) sites, summarizes the regulations governing MLLW transportation, discusses potential pretreatment, waste characterization, and repackaging requirements for MLLW that may not be readily shippable, and also reviews the uncertainties associated with public and state concerns regarding the transportation of MLLW.

TYPES AND RELATIVE DISTRIBUTION OF MLLW ACROSS DOE SITES

As per the requirements of the Federal Facility Compliance Act of 1992, the DOE is preparing a report that will list the current inventory and five-year projections at each DOE site for all types of mixed

waste, including MLLW. Preliminary estimates of the current volumes and future generation rates at each site for the different types of MLLW have already been published elsewhere (2,3). There are 12 DOE sites that account for approximately 98% percent of the volume of MLLW (3). These 12 sites are Fernald, Hanford, Idaho National Engineering Laboratory (INEL), Rocky Flats Plant (RFP), the K-25 and Y-12 sites in Oak Ridge, Oak Ridge National Laboratory (ORNL), Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory (LLNL), Paducah, Portsmouth, and the Savannah River Site (SRS). The MLLW can be generally classified into seven different types depending upon their treatment requirements (3). These seven types are aqueous liquids, organic liquids, inorganic solids, metal wastes, organic solids, heterogeneous wastes, and potential problem wastes that will require additional evaluation to incorporate them into one or more of the six other categories.

INEL has the largest current inventory of MLLW, while Y-12, SRS, and K-25 also contribute a significant portion. These four sites account for approximately 75% of the total current inventory. Similarly, INEL has the highest generation rate, followed by Y-12 and SRS. The preliminary waste stream information from each site indicates that the distribution of the types of MLLW is different for each of the 12 sites (3). For MLLW currently stored at the DOE sites, aqueous wastes have the largest inventory at ORNL and SRS; inorganic solids at Fernald, Hanford, K-25, LANL, Paducah, RFP, and Y-12; metal wastes at INEL; and heterogeneous wastes at Portsmouth. In contrast, INEL, LLNL, and Y-12 are projected to have the highest generation rates for aqueous wastes; Fernald, ORNL, and Paducah for organic liquids; K-25, LANL, and RFP for inorganic solids; Hanford for organic liquids; Portsmouth for PCB wastes; and SRS for tritium contaminated aqueous wastes. As explained later in this paper, the current inventory, generation rate, distribution, and the type of MLLW at each site will greatly influence the selection of treatment facility location.

REGULATORY FRAMEWORK FOR THE TRANSPORTATION OF MLLW

The transportation of any hazardous material involves responsibilities on the part of the generator, transporter(s), and receiving facility. Since MLLW is comprised of a radioactive component and a hazardous waste component, the regulatory requirements for transportation of MLLW appear in three separate codes of federal regulations. These include mandates by the U.S. Nuclear Regulatory Commission (NRC) to address the transportation of radioactive waste (4) (10 CFR 71), those of the U.S. Environmental Protection Agency (EPA) to address the transportation of hazardous waste (5,6) (40 CFR 262, 263), and 49 CFR 171 through 178 mandated by the U.S. Department of Transportation (DOT) to address both radioactive and/or hazardous waste shipments (7). Since the regulations do not address MLLW as a unique waste, both hazardous and radioactive properties of MLLW must be evaluated to determine the applicable regulations governing its transportation. The regulatory framework for hazardous and radioactive wastes is summarized in the next two sections, respectively.

Regulatory Framework for Transportation of Hazardous Wastes

Pre-transportation responsibilities are delegated to the generators of hazardous waste under 40 CFR 262, "Standards Applicable to Generators of Hazardous Waste" (4). Generators have full responsibility for characterizing their waste, either by analytical testing or by "applying knowledge of the hazardous characteristics of the waste in light of the materials or the processes used." As codified in 40 CFR 264.13, Resource Conservation and Recovery Act (RCRA) regulations require that an owner/operator of a treatment, storage, or disposal facility obtain a detailed chemical and physical analysis of "a representative sample" of the waste before undertaking any treatment, storage, or disposal activity (8).

However, further directives in Section 1006(a) of the RCRA (the statute) provide that the EPA or a state cannot regulate activities or substances that are subject to regulation under the Atomic Energy Act (AEA)

if the RCRA regulations are inconsistent with the AEA. Since the 40 CFR 264.13 (8) requirement could pose a hazard to occupational health and safety, it may be inconsistent with the AEA-derived requirement of maintaining exposures to radioactivity as low as reasonably achievable. A careful analysis and interpretation of these regulations will be necessary with regard to waste characterization and final treatment, storage, and disposal considerations. Although these issues may not directly address the regulatory framework regarding transportation of MLLW, they could influence the ability of DOE to prepare the MLLW for shipment.

After waste characterization and before shipment, waste generators are required by RCRA to prepare a manifest, which is identified as a "Uniform Hazardous Waste Manifest". Further, the waste must be packaged in accordance with the DOT requirements of 49 CFR 173 and 178 by labeling and marking each package in accordance with 49 CFR 172, and offering the initial transporter the appropriate placards, according to 49 CFR 172, Subpart F.

Transporters of hazardous waste are subject to guidelines (6), which require transporters to comply with the manifest system. This would include refusing hazardous waste for shipment and delivery unless accompanied by a proper manifest for the entire quantity of hazardous waste to the designated facility listed on the manifest. In the event of an accidental discharge, the transporter must take appropriate immediate action to protect human health and the environment.

The DOT regulations for labeling and marking of hazardous waste are described in 49 CFR 172. Hazard classes and divisions for hazardous materials are shown in the Hazardous Materials Table in 49 CFR 172.101. The ultimate classification of a material having more than one hazard (e.g., MLLW) is determined from the hierarchy defined in 49 CFR 173.2a. The proper packaging of hazardous materials is outlined in 49 CFR 173. The type of packaging depends on the hazard class and division assigned to the waste.

Regulatory Framework for Transportation of Radioactive Wastes

The DOT and NRC both regulate the transportation of radioactive materials. To avoid overlap and conflicting standards, an agreement was outlined in a Memorandum of Understanding between the two agencies for regulation of safety in the transportation of radioactive materials (9).

The DOT primarily regulates all aspects of the transportation of radioactive waste, as specified in 49 CFR 171 and 173. The most significant component of radioactive waste transportation is the packaging of the waste. Packaging refers to the assembly of components necessary to ensure compliance with the container integrity requirements of 49 CFR 173.403, whereas a package consists of the packaging together with its contents of radioactive material. As an example, an empty 55-gallon drum is termed "packaging", while a drum containing waste is termed a "package". Packages are designated as Type A packages, Type B packages, or packages for low specific activity (LSA) material.

Type A packages can contain waste with two upper limits for activity content of radionuclides, A_1 and A_2. A_1 is the activity limit for "special form" material, which refers to either a single solid piece or material sealed in a capsule that cannot be dispersed without destroying the capsule. A_2 is the activity limit for "normal form material", which is defined as anything that does not qualify as "special form". A significant portion of DOE MLLW is likely to be classified as "normal form". Type B packages can be used to transport high-activity low-level waste (LLW), up to 3,000 times A_1 quantities, 3,000 times A_2 quantities, or a maximum of 30,000 curies of activity, whichever is less. The values of the activity limits A_1 and A_2 are listed in a series of tables in 49 CFR 173. In general, the value of A_2 is less than A_1 indicating that a transporter can carry a greater amount of waste per package if the waste qualifies as special form.

Exemptions for low activity radioactive material are allowed by both DOT and NRC regulations. The DOT establishes two classifications for exemptions from its hazardous materials regulations. These are referred to as "limited quantity" packages falling within the limits of activities established in 49 CFR 173.423, and "low specific activity" materials. Limited quantity packages require only strong, tight packages labeled and marked as outlined in 49 CFR 173.421. These requirements are essentially the same for multiple-hazard, limited quantity radioactive materials (a category that may include MLLW), with the only difference being that the package is required to be categorized for the additional hazard (i.e., the RCRA hazardous aspect of the waste). LSA waste shipped as "exclusive use" requires only strong, tight packages, according to 49 CFR 173.425. Both limited quantity and LSA radioactive waste are exempted from the shipping paper and certification, marking, and labeling required by 49 CFR Subchapter C (Parts 171 to 180), "Hazardous Materials Regulations". However, this only applies to the radioactive aspect of the waste, not the RCRA-hazardous aspect present for MLLW.

Exemptions for low level materials are outlined by the NRC in 10 CFR 71.10. If the specific activity of a package containing radioactive material is not greater than 0.002 μCi/g it is exempt from all requirements of 10 CFR 71, including the section that requires compliance with DOT regulations. Packages containing no more than a Type A quantity of radioactive material (i.e., not exceeding the value of A_2) must only comply with the DOT regulations as required by 10 CFR 71.5. This quantity provision may account for the bulk of the MLLW shipments.

As mentioned earlier, the transportation of hazardous materials is regulated by DOT by assigning hazard classes and divisions that govern the packaging, labeling, marking, and shipping paper requirements of the materials. The hierarchy of classification for hazardous materials is established in 49 CFR 173.2a. Class 7 (radioactive materials, other than limited quantities) has the highest priority. Limited quantities of radioactive material do not carry a priority due to the regulations in 49 CFR 173.421. For MLLW, which contains limited quantities of radioactive material, the hazard class and division assigned will be based on the characteristics of the RCRA-hazardous waste. Any other MLLW will be assigned Hazard Class 7.

ACTIVITIES REQUIRED TO PREPARE UNTREATED MLLW FOR TRANSPORTATION

In order to prepare the MLLW for transportation, a number of activities may have to be performed by the DOE sites prior to transporting mixed waste. The most important of these activities that could result in a significant increase in the costs of transportation are waste characterization, pretreatment, and repackaging requirements. The extent to which these activities will be necessary at each site will be determined by the quality of data available for the waste, quality of existing packaging, and inventory of MLLW that is not readily shippable. Each of these requirements is discussed below.

Waste Characterization

The manifest system of RCRA and the packaging requirements of the DOT both require specific information about the waste to accompany the shipment. For example, the shipper must identify the DOT hazard class and select a proper shipping name using hazard class criteria found in 49 CFR 173 and the Hazardous Materials Table in 49 CFR 172.101. If multiple hazards are present, the shipper must use the hierarchy tables in 49 CFR 173.2 to determine the correct hazard class. The proper shipping name must accurately describe the waste and also correspond to the hazard class from the 49 CFR 173.2 hierarchy list. As a result, for materials that exhibit multiple hazards (such as mixed waste), it is extremely important for the shipper to characterize the waste in order to determine proper packaging requirements.

Information required for transportation typically includes radiological characterization, and adequate

characterization of hazardous constituents to satisfy the requirements of the Uniform Hazardous Waste manifest. Complete radiological characterization of the waste is preferable because inadequate characterization forces the shipper to use conservative assumptions for the package selection process. This will decrease the amount of waste that can be shipped per package and thus increase the number of shipments. The waste characterization process will be dictated primarily by RCRA, which calls for a detailed analysis of a "representative sample" of the waste. Since it may be difficult to obtain "representative" samples from MLLW that consists of either inorganic solids or heterogeneous wastes, this may hinder the ability of sites having a large inventory of such wastes to become a shipping site. Waste characterization may be performed either by process knowledge or by analytical testing. Waste characterization may also be required to verify the absence of items such as pyrophorics and compressed gases that may be prohibited from transportation.

Pretreatment of MLLW Prior to Transportation

Wastes that may require pretreatment prior to transportation include liquids, and wastes containing prohibited items like pyrophorics, explosives, and compressed gases. Although the transportation of liquids is not prohibited, the DOT packaging restrictions can substantially increase if the waste does not qualify as LSA material. For example, if a Type A package is used to transport liquid waste above LSA limits, the mechanical strength of the package should be sufficient to withstand a 30-ft drop test (instead of the usual 4 ft for solids) and also contain adequate absorbent to absorb twice the volume of liquid in the package. This has major implications for sites such as ORNL and SRS that have a large inventory of liquid waste, because the ability of these sites to ship waste to a centralized facility will greatly depend on the quantity of radioactivity in the liquids. Similarly, if waste characterization reveals that any prohibited items are present in the waste, the waste has to be processed to ensure that the prohibited items are not transported. Sorting operations may also be needed to prevent incompatible items from being transported in the same container.

Repackaging of MLLW Prior to Transportation

Repackaging of MLLW may be required prior to transportation for three different reasons. Any MLLW in containers that may have corroded or been damaged due to extended storage will have to be repackaged into new containers. Also, any MLLW that is currently stored in odd-shaped or odd-sized containers would also have to be repackaged to meet DOT specifications. Repackaging may also be necessary because of limitations on the quantity of radioactivity that can be transported in a Type A package. For example, if radiological characterization shows that the total activity in a Type A container exceeds the value of A_2 for the radionuclide, then the contents of the container would have to be divided between one or more additional containers until the A_2 limits are met for each package. This will increase the number of shipments and thus increase transportation costs.

UNCERTAINTIES OF PUBLIC AND STATE ACCEPTANCE OF MIXED WASTE TRANSPORTATION

Perhaps the most important aspect of mixed waste transportation may be the uncertainties associated with public and state government acceptance of radioactive waste shipments through their state boundaries. Public concerns and information exchange have been the subject of discussion for many publications in the past (10-13). In a joint study done by the Oregon Department of Energy and the Oregon State University, a majority (55.7%) of the respondents felt that the risks of transportation are greater than the risks of continued storage of radioactive waste at Hanford (10). Also, a significant majority of those surveyed were concerned about health and safety effects in their local area. In a similar vein, several Indian tribes have expressed concerns over the potential environmental, health, and safety risks of transporting transuranic wastes to the Waste Isolation Pilot Plant (WIPP) in New Mexico (11). The DOE has sought to identify these concerns and concluded that an appropriate response to tribal concerns will

depend both on understanding tribal interests and also the specific issues that are accorded top priority by individual tribes (11).

A number of interesting findings have also been reported with respect to public information and communication for the transportation of radioactive materials (12). Notable among these are that the public is genuinely concerned about safety, providing the public with technical facts is not enough, and also that the public normally likes to know "how is something safe" instead of being told that "it is safe". The results of a 1989 interactive meeting between DOE representatives and over 20 local government officials from around the U.S. also yielded interesting results (13). In this meeting, the local officials wanted to see DOE work with their membership organizations and propose legislation related to nuclear and hazardous materials transportation. Another suggestion was to establish a Nuclear Transportation Advisory Committee made up of interested Federal agencies, States, and local governments.

In addition to the costs of resolving potential problems associated with public and state government opposition, transportation costs could escalate if a state demands an appropriate amount of monetary compensation for improving their infrastructure system (such as highways). An example of a State demanding such an "impact cost" is the State of New Mexico which is scheduled to receive money from DOE to improve and maintain its highways for the transportation of transuranic waste to WIPP. Also, for planned centralized treatment facilities, the costs and schedules for obtaining permits for a centralized facility may be an expensive and lengthy process because of the local community perception that their location is being chosen as a "sacrifice area". However, it seems that although public and state acceptance of mixed waste transportation are by no means guaranteed, a helpful information exchange program for the public in combination with local government participation in decision making will definitely improve the chance of acceptance.

SUMMARY AND CONCLUSION

This paper has explored various issues that will influence the shipment of MLLW and will also have an effect on the decision to centralize treatment facilities. Many trade-offs are involved in the decision making process and therefore the benefits of centralization or regionalization should be carefully evaluated against their disadvantages.

The anticipated benefits from centralization or regionalization of MLLW treatment facilities will include cost reduction due to economies of scale, standardization of permitting activities, and lesser number of permits required. On the other hand, the disadvantages of centralization include the cost of transportation itself, cost of any waste characterization, pretreatment, or repackaging activities that may be required prior to shipment, the risks associated with transportation, "impact" costs demanded by State governments, public and State opposition to transportation, and also the public perception of being a resident of a "sacrificial area" or a "dumping ground". Since both heterogeneous wastes and liquids may pose problems for transportation, it may help to designate sites with high volumes of these wastes as receivers instead of shippers. Also, one other option may be to minimize both the amount and the distance of transportation by locating two regionalized facilities, one in the east and the other in the west. As can be seen from the list of disadvantages, not all of the attributes can be quantified. However, many of these can be estimated based on prior experience. In summary, although the initial argument of economies of scale seems attractive in favor of centralization of treatment facilities, there are many disadvantages associated with centralization that need to be quantified and resolved before the best approach can be chosen.

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REQUIREMENTS FOR SHIPMENT OF DOE RADIOACTIVE MIXED WASTE

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ABSTRACT. The experience outlined in this paper will provide some practical insight on the preparations required to obtain permission to ship mixed waste from ANL-E to Westinghouse Hanford Company (WHC) located in Richland, Washington.

Since this material is generated within a DOE operated Laboratory, all procedure require that DOE orders be followed. In this example the source of the mixed waste was a waste matrix representing sludge, not solids, from several storage tanks, including acid waste tanks, IOMEX/FLOC tanks, evaporation feed tanks and waste storage tanks.

In order to ship mixed waste to Hanford for storage by Westinghouse Hanford Company, ANL-E was required to pass a full scale audit and prepare a request for a WHC Storage Disposal Approval Record (SDAR). The request for SDAR required complete characterization of all radioactive isotopes and the hazardous constituents. Many of the wastes were land ban and included D, F, & W waste codes.

The types of packaging presentation will discuss the history of their proper procurement through the special treatment to turn a sludge into a shippable and acceptable solid, prior to sending the truck out of the gate.

INTRODUCTION OF WASTE STREAMS

Since the beginning of operations at Argonne National Laboratory, from the period roughly five years after the end of World War II up to the present, large quantities of radioactive mixed waste (RMW) have been generated. Due to the nature and variety of experiments, this waste is composed of a large number of chemical compounds and radionuclides. For example, Building No. 200, dedicated entirely to chemistry, encompasses an area of roughly six acres or slightly less than of 300,000 ft.^{2} (27,000 m^2).

There are also Chemical Technology, Biology, and other buildings dedicated to high-energy physics and research, which are also major generators of radioactive mixed waste (RMW).

There are several sources of RMW which, in the past, were collected at waste tanks and/or sludge tanks. They were eventually pumped out by special pumps and processed in an evaporator located in the waste operations area in Building No. 306. Some of this radioactive mixed waste represents pure elementary mercury. Comments by the workers responsible for the cleanup of the original suggest "buckets of pure mercury", probably left over from broken monometers and thermometers. These cleaning tanks must be manually cleaned up because the RMW material was too dense to pump with the equipment in use.

The four tanks being discussed here are located in Building No. 306. They are the Acid Waste Tank, IMOX/FLOC Tanks, Evaporation Feed Tanks, and Waste Storage Tanks. All of these tanks are

characterized and handled separately. This paper discusses the process and the requirements for characterization and the associated paperwork.

DOE ORDERS PREVAIL

In order to begin the process of storage or disposal of RMW, DOE Order 5820.2A, entitled Radioactive Waste Management, dated September 26, 1988, must be followed. This DOE Order states specifically that Westinghouse Hanford Company located in Richland, Washington is the only available source of storage to Argonne National Laboratory-East, which is located near Chicago, Illinois.

AUDIT REQUIREMENTS

In order to discuss the possibilities of shipping waste to Westinghouse Hanford Company for storage, Argonne National Lab was required to invite auditors from Westinghouse Hanford Company to perform a complete audit. After ANL-E passes the audit, we can be certified to ship both low-level waste (LLW) and RMW to Westinghouse Hanford Company.

The first process was LLW, from a Decontamination & Decommissioning project. Beginning in late May 1992, Argonne National Lab was approved by Westinghouse Hanford Company to ship both LLW and RMW to its facility: in the case of LLW for burial, and in the case of RMW, for storage.

This audit process must be repeated on an annual basis, and thus, in May 1993, Argonne National Laboratory was again audited. The 1993 audit was called an assessment and included some training. Argonne has maintained its level of quality assurance as well as 100% sorting inspection and continues the same relationship with Westinghouse Hanford in regard to LLW and RMW certification.

CHARACTERIZATION

The specific process for shipping RMW from the various tanks starts with a complete characterization of the waste constitutents, as well as various radionuclides. Included is the Toxicity Characteristic Leachate Procedure (TCLP), an expensive process which must be done before various forms are completed. The request for a shipment of RMW is really a request for storage.

It is important to point out here that RMW storage facilities vary in size; the storage facilities at Hanford, Washington comprise an area which could easily accommodate four or five soccer playing fields. The facilities are large, well maintained, and are new buildings. Without access to Hanford, ANL-E would have a difficult time disposing of mixed waste elsewhere within the DOE system.

PLANNING FOR THE SHIPMENT

The process starts with a Waste Storage Disposal Request (WSDR) form (Appendix I), which must be completed before requesting a Storage/Disposal Approval Record (SDAR) (Appendix II).

The WSDR is filled out for each waste stream. Then, after internal discussion and review by the Westinghouse Hanford personnel, the SDAR is sent through normal channels, passing from the DOE-Richland Operations Office to the DOE-Chicago Operations Office, to the DOE-Argonne National Laboratory Area Office, to Waste Management Operations at Argonne National Laboratory through the Environment and Waste Management Program. The approval process appears to be somewhat cumbersome,

although it provides a pathway to determine future disposal requirements at the Hanford facility, as well as several control points.

Once the SDAR is received by Waste Management, the planning for converting a mixed waste sludge into an acceptable solid mixed waste can begin.

The packaging involves a DOT 7A Type A Specification 17C galvanized 55 gallon drum (1). In addition, the packaging system requires a secondary containment for liquid RMW in the form of absorbed sludge. The secondary containment must be a 90 mil high density polyethylene (HDPE) rigid liner. In addition, a small amount of liquid absorbent must be placed between the 90 mil liner and the drum. The certified absorbents identified by the Westinghouse Hanford Company are found in a well documented book (2).

MARKING AND LABELING

The SDAR also provides the necessary information on marking and labeling. In our case, after RMW was placed in the drum and inside the liner, we felt it advisable to invite a member of the Westinghouse Hanford Company group, which specializes in labeling and marking, to visit the Laboratory and review the work.

The marking and labeling requirements are outlined on the SDAR. In addition, we closely followed the guidelines of the U.S. Department of Transportation (DOT), Regulations for Marking and Labeling (3), and the Washington State Dangerous Waste Regulations (4).

DOCUMENTATION FORMS

The next step for shipment is the preparation of documentation forms. Both a Low-Level Waste Storage/Disposal Record (LLWSDR) (Appendix III) and a Radioactive Mixed Waste Attachment Sheet (RMWAS) (Appendix IV) are required prior to shipment.

The next documentation step is the Preparation of the Storage Record, which is necessary only for RMW. In the case of LLW, a burial record is needed and is somewhat easier to complete.

The complexities of characterization and shipping of chemical (hazardous) waste can lend themselves to a frustrating experience. It involves not only a higher level of difficulty than often imagined, but it takes far more time than anticipated. The shipping papers include a Uniform Hazardous Waste Manifest (Appendix V). These records are extremely difficult to prepare and to be accurate. The Straight Bill of Lading (Appendix VI) also has attachments: (1) Land Disposal Restriction Notice; (2) a list of radionuclides; (3) a list of the external radiation; (4) U.S. Department of Energy Instructions regarding controls for radioactive shipments consigned as Exclusive Use (sole use or full load); and (5) ANL-E Emergency Response Guide No. 62.

The protocol involves calling Westinghouse Hanford Company, notifying them that the shipment has left ANL-E, and asking the truckers leaving with the RMW when the shipment is expected to arrive at its destination. Normally, the information is faxed to an individual who will handle coordination at the Westinghouse Hanford TSD site.

CONCLUSION

From start to finish it took slightly over nine months from the initial request to final storage of this RMW at Richland, Washington. The documentation phase of this shipment required approximately 120 person-hours. Plan ahead and start early.

ACKNOWLEDGEMENT - Argonne National Laboratory is operated by the University of Chicago for the U.S. Department of Energy, under Contract W-31-109-ENG-38.

The authors wish to acknowledge the cooperation and input of Mr. Jim Eide, whose knowledge of operations at the Argonne National Laboratory has been beneficial to this packaging and shipping operation.

REFERENCES

1. DOT (U.S. Department of Transportation), Shipping Container Specifications, 49 CFR 178, U.S. Government Printing Office, Washington, DC (1992).
2. WHC (Westinghouse Hanford Company), Hanford Site Solid Waste Acceptance Criteria, WHC-EP-0063-3, WHC, Hanford, WA (1991).
3. DOT (U.S. Department of Transportation), Hazardous Materials Tables and Hazardous Materials Communication Regulations, 40 CFR 172, U.S. Government Printing Office, Washington, DC (1992).
4. Washington State Department of Ecology, Washington State Dangerous Waste Regulations, WAC 173-303, Olympia, WA (1991).
5. ANL (Argonne national aboratory), Emergency Response Guide N-62, ANL, Argonne, IL (1992).

APPENDIX I

WASTE STORAGE/DISPOSAL REQUEST (REV 0, 9/1/91)

COMPLETE AND SUBMIT TO: SOLID WASTE ENGINEERING (SWE); N3-11/WHC; P.O. BOX 1970; RICHLAND, WA 99352. FOR DETAILS REFER TO WHC-EP-0063

WHC Tracking #

Company: Argonne National Laboratory 9700 S. Cass Avenue Argonne, IL 60439	Qualified Generator/MSIN M. A. Sedaro, Manager EWM/WMO - Building 306	Accumulation Date (If Applicable) N/A
Approved Generating Facility (Per Cert. Plan) Argonne National Laboratory - East	Signature/Date	Phone (708)252-5565
Generator Log Number/Tracking Number	Request Includes: X Attachment A (For Low-Level, RMW, TRU, and High-Level) __ Attachment B (For On-Site Non-Radioactive Waste ONLY)	

Waste Type

(Mark all that apply)

X Low-Level	__ Classified	X RMW	__ Compactible
__ Transuranic	__ Non-Radioactive	__ High-Level	X Contact Handled
__ > Class C	__ Remote Handled	__ Heat Generating Potential	__ Gas Generating Potential

Additional Information for Low-Level, RMW, TRU, And High-Level Waste ONLY

General Waste Description: STORAGE TANK SLUDGE WASTE collected at the bottom of the tanks that are used to store low-level liquid waste before it is processed futher in the evaporator. Sludge waste is absorbed using enough cellulose corn cob to absorb twice the amount of liquid present.

Physical Properties
- __ Solid
- __ Solidified
- X Absorbed Liquids (Sludge)
- __ Labpacked Free Liquids

pH 9 Flashpoint _____ °F

Hazards _____

Transport Category (Mark all that apply)
- __ < 2 nCi/g
- __ Limited Quantity
- X Low Specific Activity
- __ Type A __ Type B
- __ Highway Route Control
- __ SARP #_____

Special Package Form
- __ Lab Pack
- X Disposable Overpack COC #_____
- __ Returnable Overpack COC #_____
- __ Liner (____) mils

PIN (Specific Shipment): _____

Container Information

External Dimensions: DOT 7A Type A specification 17C galvanized 55-gallon drums 24" dia./35" high

Maximum Gross Weight: 900 lbs or in accordence with latest DOT 7A spec.

Drawing/Specification Number: DOT spec. 17C (see 49CFR 178.115)

General Description: constructed to DOT specification for 55 gallon removable head 17C galvanized steel drums (see 49CFR 178.115). Drums containing absorbed sludge will have 90 mil high density polyethylene (HDPE) rigid liner with absorbent material placed between the liner and the drum.

Closure Mechanism: constructed to DOT specifications for 55 gallon removable head 17C galvanized steel drums (see 49CFR 178.115)

Special Rigging Requirements: _____

ATTACHMENT A (REV 0, 9/1/91)
Radioactive Stream Characterization

Radionuclides	*Nano cf/g	Waste Components	Wt %
Carbon-14	LSA	PCBs zero ppm	N/A
Iodine-129	LSA	Asbestos	None
Technetium-99	LSA	Chelating Agents: (List)	No
Tritium: ☐X ≤ 20 mCi/m³ ☐ > 20 mCi/m³			
Others: (List)			
Acid Waste Tank A,B		Ion Exchange Resins: (List)	No
Cs-137	8.0		
Co-60	1.4		
AM-241	6.5	Lead Shielding	No
Sb-125	.2	Lead Waste	No
Np-237	.2	Solvents: ☐ Old ☐ Used (List)	
Na-22	.01		
gross Alpha	12.7		
gross Beta	26.8		
IFT -A,B,C			
Cs-137	33.3	Others (List)	
Co-60	12.7	IFT,EFT tanks	
Am-241	12.8	H2O (Water)	52.6
Sb-125	0.5	Carbonaceous material	12.9
Np-237	0.9	Ash	34.4
Na-22	NCD	Residue	2
gross-Alpha	20.0	(Residue after treatment of ash portion	
gross-Beta	127	w/HNO3/HF/HCL)	2.65
		Total	100
Contd. next page		Contd. next page	
		Total (Must Equal 100%)	

ATTACHMENT A (REV 0, 9/4/91) Radioactive Stream Characterization			
Radionuclides	Nano Ci/g	Waste Components	Wt %
EFT - A,B,C			
Cs-137	.9	WST	
Co-60	.2	H2O (Water)	56.6
Am-241	.2	Carboneceous material	10.7
Sb-125	.02	Ash	32.7
Np-237	NCD	Residue (insoluable)	1.40
Na-22	NCD	Residue after treatment of ash portion w/HNO3/HF/HCL	
gross Alpha	.12	mixture	100
gross Beta	2.0		
WST - A,B,C			
Cs-137	6.8		
Co-60	5.5	AWT	
Am-241	3.7	H2O (Water)	77.1
Sb-125	1.0	Carboneceous material	5.97
Np-237	.2	Ash	16.9
Na-22	NCD	Residue (insoluable)	1.05
gross Alpha	6.2	Residue after treatment of ash portion w/HNO3/HF/HCL	
gross Beta	47	mixture	100
* NCD = No counts detected			
Total		Total (Must Equal 100%)	

RADIOACTIVE MIXED WASTE ATTACHMENT SHEET (REV 0, 9/1/91)		1. Page 1 of 2
2. PIN	3. Manifest No.	4. Manifest Date
5. ☒ Land Disposal Restricted Source of Restriction ☒ RCRA, ☒ F-Listed, ☒ EHW		6. Waste Designation ☒ EHW ☐ DW
7. Waste numbers that apply to this package: D004 through D011, D036, F001 through F003, F005		

WASTE DESCRIPTION

8. Hazardous Constituent	9. Weight (kg)	10. Physical Properties
Arsenic	0.392	Sludge in AWT Tanks
Barium	1.277	"
Cadmium	.410	"
Chromium	104.8	"
Lead	12.17	"
Mercury	4.879	"
Selenium	0.316	"
Silver	0.169	"
Nitro Benzene	0.310	"
Acetone	0.1312	"
MEK	0.0057	"
Trichloroethene	0.0568	"
Tetrachloroethene	8.744	"
Toluene	0.0227	"
Xylene	0.0437	"
Arsenic	0.023	Sludge in IFT Tanks
Barium	0.578	"
Cadmium	0.461	"
Chromium	13.04	"
Lead	2.699	"
Mercury	2.289	"
Selenium	0.091	"
Silver	0.059	"
Nitro Benzene	0.026	"
Methylene Chloride	0.00052	"
Acetone	0.00017	"
Benzene	0.00031	"

RADIOACTIVE MIXED WASTE ATTACHMENT SHEET (REV 0, 9/1/91)		1. Page 2 of 2
2. PIN	3. Manifest No.	4. Manifest Date
5. ☒ Land Disposal Restricted Source of Restriction ☒ RCRA, ☒ F-Listed, ☒ EHW		6. Waste Designation ☒ EHW ☐ DW
7. Waste numbers that apply to this package: D004 through D011, D036, F001 through F003, F005		

WASTE DESCRIPTION		
8. Hazardous Constituent	9. Weight (kg)	10. Physical Properties
Arsenic	0.041	Sludge in WST tanks
Barium	0.488	" "
Cadmium	0.168	" "
Chromium	15.56	" "
Lead	1.933	" "
Mercury	1.027	" "
Selenium	0.125	" "
Benzene	0.066	" "
Methylene Chloride	0.00043	" "
Acetone	0.00089	" "
MEK	0.00052	" "
Tetrachloroethene	0.00023	" "
Arsenic	0.0002	Sludge in EFT tank
Barium	0.0025	" "
Cadmium	0.0009	" "
Chromium	0.035	" "
Lead	0.0084	" "
Mercury	0.03	" "
Selenium	0.0005	" "
Nitro Benzene	2.098	" "
Methylene Chloride	0.00024	" "
Acetone	0.0142	" "
MEK	0.0079	" "
Tetrachloroethene	0.0011	" "
Ethyl Benzene	0.00012	" "
TOTAL WEIGHT (Kg)		
11. Estimated Liquid Volume (Liters)		

LOW-LEVEL WASTE STORAGE/DISPOSAL RECORD (REV 0, 9/1/91) | 8. PAGE 1 OF _____

Storage/Disposal Site Information

I certify that a physical inspection of the waste package to the extent possible and a cross check of the applicable documentation have been performed in accordance with SW-100-050 or SW-100-110.

2. Signature-Acceptance | Date

3. Area | 4. Facility | 5. Unit

6. Storage Location (SO1)

Module | Tier | Position

7. Disposal Location

Beginning Coordinates N W

Ending Coordinates N W

REFERENCES

16. RSR No | 17. SDAR No.

18. DOE/NRC 741 No. | 19. PDR No.

1. SWSDR No. (DO NOT WRITE IN THIS SPACE)

9. PIN

10. Waste Generator

11. Charge Code, SO No., or MPO No.

12. WRM No.

13. Name of Contact

14. Address/Phone

I certify that: (1) No capital property is included in this waste unless documented by a Property Disposal Request and described below. (2) To the best of my knowledge, the information entered below is complete and accurate, and the waste package is in compliance with WHC-EP-0063 and the Storage/Disposal Approval Record (SDAR). (3) Unless designated a Radioactive Mixed Waste (RMW), this waste is not a dangerous waste as defined by Chapter 173-303 WAC or other applicable state or federal regulation governing the management of hazardous waste. (4) The charge code is correct.

15. Signature | Date

20. Waste Designation ☐Category 1 ☐Category 3 ☐>Category 3 ☐RMW ☐Classified

21. Point of Origin

22. Container Type | 23. LxWxH or DxL

24. Cont. Vol. (m^3) | 25. Tare Weight (kg)

26. Date Packaged | 27. Gross Weight (kg)

30. Waste Category (Check One)
☐ SW ☐ DS
☐ DD ☐ NC
☐ CE ☐ SS

31. Waste Code (Check one)
☐ FW ☐ HM ☐ CL ☐ WD
☐ SL ☐ GL ☐ CM ☐ TW
☐ DM ☐ SO ☐ PB ☐ NC
☐ LM ☐ PA

28. Thermal Power _____ ☐ <0.1 W/ft³

29. Dose Rate (mrem/hr)_____ at _____

32. Seal No.

WASTE CONTENTS DESCRIPTION

33. Article Description	34. Estimated Volume %	35. Est. Weight (kg)	36. Radio-nuclide	37. Curies (Fission/Activation Products only)	38. Weight (g) (TRU, Uranium, and Thorium only)
39.TOTAL			TOTAL		

ATTACHMENT B (REV 0, 9/1/91) Non-Radioactive Waste Items List										WHC Tracking #
A Item No.	B Number of Containers	C Container Description	D Kg Waste	E Waste/Process Description	F Chemical Components	G Weight %	H Physical Properties	I Hazards	J Waste Status	K Cont. Status

APPENDIX II

STORAGE/DISPOSAL APPROVAL RECORD
FOR RADIOACTIVE SOLID WASTE

SDAR Number: 60-1G-6AM-0301

This is a Multiple Use SDAR

Prepared by: [signature] Approved by: [signature]
Date: 11/9/92 Date: 11/9/92

Reviewed by: [signature] Approval Status: Approved
Date: 11-9-92

Waste Generator: Argonne National Laboratory

Waste: LLW-Mixed Waste - Aqueous Liquids (Absorbed)

Storage/Disposal Container: DOT 17C 55-Gallon Galvanized Drum with a 90-mil High Density Polyethylene (HDPE Liner)

References:
1. Manual, N.P. Willis, "Hanford Site Solid Waste Acceptance Criteria," WHC-EP-0063, Revision 3.
2. Reference Letter: 9207016 Dated: 9/23/92
3. Request #: 21302
4. Generator Letter #: 92-SWT-413

HANDLING RESTRICTIONS:

Contact, Land Banned

MAXIMUM TRANSPORT CATEGORY:

Low Specific Activity

CONTAINER APPROVAL:

- U.S. Department of Transportation

DISPOSITION INSTRUCTIONS:

- Notify Operations Management if a waste package contains more than one gram of fissile material
- The waste will be stored or disposed as follows:

  Waste Category 1
  CWC - Other RMW Storage

WASTE DESCRIPTION:

1. Waste May Include:

   - Category 1 Waste
   - Land Ban
   - Absorbed Aqueous Liquid
   - F Listed Waste
   - Lead Waste
   - Mercury
   - C-14, I-129, Tc-99

2. Description of Waste Matrix: Radioactive solid waste containing sludge from the Acid Waste Tanks (AWT) A, B; IONEX/FLOC Tanks (IFT) A, B, C; Evaporation Feed Tank (EFT) A, B, C; and Waste Storage Tanks (WST) A, B, C. Free liquids are not allowed under this SDAR.

   The generator is responsible to ensure that the waste contains no hazardous constituents (as defined in WAC 173-303) other than those listed in item 4 of the SDAR.

3. Radioactive Material Description:

   Low-Level: C-14, I-129, Tc-99, Cs-137→Ba-137m, Co-60→Ni-60m, Am-241, Sb-125→Te-125, Np-237, Na-22

   Transuranic: <100 nCi/ gram

4. Hazardous Constituents Description: acetone, lead, mercury, arsenic, cadmium, chromium, selenium (Land ban: D004, D006, D007, D008, D009, D010). In addition to the above Hazardous Constituents Description, the following apply:
   AWT: toluene, xylene, silver, methyl ethyl ketone, trichloroethylene, nitrobenzene, barium (Land ban: D005, D011, D040, D036).
   WST: tetrachloroethylene, methyl ethyl ketone, methylene chloride, benzene barium (Land ban: D005, D018).
   EFT: tetrachloroethylene,methyl ethyl ketone, nitrobenzene, methylene chloride, ethylbenzene (Land ban: D036, D039).
   IFT: tetrachloroethylene, silver, nitrobenzene, methylene chloride, benzene, barium (Land ban: D005, D011, D036).

5. Maximum Allowable Fissile Quantity: <1 g fissile material

6. Void Space Filler Material: n/a

PACKAGING DESCRIPTION:

1. Container: DOT 17C 55-Gallon Galvan 1 Drum with a 90-mil HDPE Liner

2. Drawing/Specification Number: DOT Specification 17C

3. External Dimensions: 24" diameter x 35" high (61cm x 89cm)

4. Disposal Volume: 7.4 cubic feet (0.2 cubic mater) per drum

5. Maximum Gross Weight: 1000 pounds (454 Kg) per drum

6. General Description: DOT 17C 55-gallon galvanized steel drum, gasketed drum lid, locking ring, and locking ring nut.

7. Required Internal Packaging: The drum will be lined with a 90-mil HDPE liner. A layer of diatomaceous earth will be placed between the bottom of the drum and liner. A superabsorbent polyacrylate polymer, RADPADS Granular from Environmental Scientific Inc. or equivalent, will be mixed thoroughly with the waste. The absorbent will be sufficient to absorb twice the volume of liquid potentially present. Sufficient headspace to accomodate expansion due to freezing shall be left in the drum. Sharp objects must be padded or otherwise protected to prevent damage to the liner.

8. Closure Mechanism: The liner lid will be secured to the liner and sealed. The drum closure will be secured by a gasketed drum lid, locking ring, and locking ring nut. The locking ring nut will be torqued and a lock nut applied.

9. Maximum Allowable Radiation Levels:

   Contact: <100 mRem/hour max

   Remote: n/a

10. Maximum Allowable Surface Contamination:

    <220 dpm/100 square centimeters alpha
    <2200 dpm/100 square centimeters beta-gamma

11. Description of Returnable Transport Overpacks: n/a

12. Required Labels/Markings: Marking, labeling, and placarding as required by DOT in addition to the following:

Top & Side: WRM Number
Top & Side: Package Identification Number
Top & Side: Gross Weight in Pounds
Side: DOT Radioactive Label or Equivalent
Side: "Land Disposal Restricted" Marking
Side: "RMW-EHW" Marking
Side: "Waste Category 1" Marking
Side: "Toxic" Marking
Side: "Carcinogen" Marking
Side: "Persistent" Marking
Side: Hazardous Waste Sticker with Waste Codes: WT02, WC02, D006, D007, D008, D009, F001, F002, F003, F005
In addition to the above codes, the following apply:
AWT: D004, D005, D010, D011, D036, D039, D040, WP02, F004
WST: D004, D005, D010, D018,
EFT: D036, D039
IFT: D004, D005, D010, D011, D036

RQ for D004, D008, D009 is 1 lb.
RQ for D018, D006, D007, D010 is 10 lbs.
RQ for D039, D040 is 100 lbs.

ADMINISTRATIVE CONTROLS:

- A Low-Level Waste Storage/Disposal Record (LLWSDR) form and Radioactive Mixed Waste Attachment Sheet (RMWAS) are required for each waste package
- A waste inventory will be maintained by the generator.
- Each waste package will be inspected after packaging to verify that it is in good condition with no breach of containment.
- No free liquids are allowed under authority of this SDAR.
- The surface radiation dose rate for any one contact handled package may not exceed 100 mRem/hr at any point without approval of Solid Waste Operations before shipment.
- Quantify radionuclides on the LLWSDR and hazardous components on the RMWAS for each waste package.
- This waste must comply with the generator Waste Certification Plan.
- Requirements of WHC-EP-0063-3 apply unless otherwise stated in this SDAR.

APPENDIX III

LOW-LEVEL WASTE STORAGE/DISPOSAL RECORD
(Rev 0, 9/1/91)

a. Page 1 of 2

Storage/Disposal Site Information

I certify that a physical inspection of the waste package to the extent possible and a cross check of the applicable documentation have been performed in accordance with SW-100-060 or SW-100-110.

2. Signature-Acceptance | Date

3. Area | 4. Facility | 5. Unit

6. Storage Location (SOI)

Module | Tier | Position

7. Disposal Location

Beginning Coordinates N W

Ending Coordinates N W

REFERENCES

16. RSR No.

17. SDAR No. 60-1G-6AM-0301

18. DOE/NRC 741 No. NA

19. POR No.

1. SWSDR No. (DO NOT WRITE IN THE SPACE)

9. PIN ANL93-MW-00047

10. Waste Generator ARGONNE NATIONAL LABORATORY

11. Charge Code, SO No., or MPO No. MPO No. 061217

12. WRM No. 9304-10-0047

13. Name of Contact JOHN HERMAN

14. Address/Phone No. ARGONNE, IL 60439 (708)252-6348

I certify that: (1) No capital property is included in this waste unless documented by a Property Disposal Request and described below. (2) To the best of my knowledge, the information entered below is complete and accurate, and the waste package is in compliance with WHC-EP-0063 and the Storage/Disposal Approval Record (SDAR). (3) Unless designated a Radioactive Mixed Waste (RMW), this waste is not a dangerous waste as defined by Chapter 173-303 WAC or other applicable state or federal regulation governing the management of hazardous waste. (4) The charge code is correct.

15. Signature [signature] Date 4/23/93

20. Waste Designation ☐ Category 1 ☐ Category 3 ☐ >Category 3 ☒ RMW ☐ Classified

21. Point of Origin

22. Container Type 55 GAL. DRUM | 23. LxWxH or DxL NA

24. Container Volume (m^3) 0.2 | 25. Tare Weight (kg) 27.7

26. Date Packaged 03/15/93 | 27. Gross Weight (kg) 200.0

30. Waste Category (Check one)

☐ SW ☐ DD
☐ CE ☐ NC
☐ DS ☒ SS

31. Waste Category (Check one)

☐ CL ☐ GL ☐ PA ☐ SO
☐ CM ☐ HM ☐ PB ☐ TW
☐ DM ☐ LM ☒ SL ☐ WD
☐ PW ☐ NC

28. Thermal Power _____ ☒ <0.1 W/m^3 | 29. Dose Rate (mrem/h) 47.0 at 2.5 cm | 32. Seal No.

WASTE CONTENTS DESCRIPTION

33. Article Description	34. Estimated Volume (%)	35. Estimated Weight (kg)	36. Radionuclide	37. Curies (Fission/Activation Products only)	38. Weight (g) (TRU, Uranium, and Thorium only)
90-mil HDPE Liner	4.0	5.0	Am-241		5.9E-04
SOLIDIFIED SLUDGE(from IFT)consiting of:			Np-237		2.0E-01
NON-HAZARDOUS CONSTITUENTS	89.5	155.9	Cs-137	5.3E-03	
HAZARDOUS CONSTITUENTS	2.0	3.4	Ba-137	5.3E-03	
ABSORBENT (radsorb)	3.0	5.0	Co-60	2.0E-03	
PLASTIC (bags)	0.5	1.0	Ni-60m	2.0E-03	
CLOTH (rags)	0.5	1.0	Sb-125	7.9E-05	
ABSORBENT (wyk)	0.5	1.0	Te-125	7.9E-05	
39. Total	100	172.3	Total	1.9E-02	2.0E-01

A-6000-840 (11/91)

APPENDIX IV

RADIOACTIVE MIXED WASTE ATTACHMENT SHEET
(Rev 0, 9/1/91)

1. Page 2 of 2

2. PIN	3. Manifest No.	4. Manifest Date
ANL93-MW-00047	10001	04/26/93

5. [X] Land Disposal Restricted — Source of Restriction: [X] RCRA, [X] F-Listed, [X] EHW

6. Waste Designation: [X] EHW [ ] DW

7. Waste Nos. that apply to this package: D004, D005, D006, D007, D008, D009, D010, D011, D036, F001, F002, F003, F005, MT02, MC02

WASTE DESCRIPTION

8. Hazardous Constituent	9. Weight (kg)	10. Physical Properties
Arsenic	4.0E-03	SLUDGE IN IFT TANKS
Barium	1.0E-01	
Cadmium	8.0E-02	
Chromium	2.3	
Lead	4.7E-01	
Mercury	4.0E-01	
Selenium	1.6E-02	
Silver	1.0E-02	
Nitrobenzene	7.3E-03	
Methylene Chloride	4.0E-04	
Acetone	1.3E-04	
Benzene	5.6E-05	
Total Weight (Kg)	3.4	

11. Estimated Liquid Volume (Liters) 150

A-6000-839 (11/91)

APPENDIX V

STATE OF ILLINOIS ENVIRONMENTAL PROTECTION AGENCY DIVISION OF LAND POLLUTION CONTROL

P.O. BOX 19276 SPRINGFIELD, ILLINOIS 62794-9276 (217) 782-6761

FOR SHIPMENT OF HAZARDOUS AND SPECIAL WASTE

State Form LPC 62 8/81 IL532-0610

PLEASE TYPE (Form designed for use on elite (12-pitch) typewriter.) EPA Form 8700-22 (Rev. 6-89) Form Approved. OMB No. 2050-0039. Expires 9-30-

UNIFORM HAZARDOUS WASTE MANIFEST

1. Generator's US EPA ID No.: IL3890008946 | Manifest Document No.: 10001

2. Page 1 of 1 | Information in the shaded areas is not required by Federal law but is required by Illinois law

3. Generator's Name and Mailing Address | Location If Different
ARGONNE NATIONAL LABORATORY ATTN: John Herman
9700 South Cass Avenue, Bldg. 306, Argonne, IL 60439

A. Illinois Manifest Document Number: IL 4765488 | Fee Paid, if Applicable

4. 24 HOUR EMERGENCY AND SPILL ASSISTANCE NUMBERS: (708)252-6130

B. Illinois Generator's ID: 1 0 4 3 8 0 2 0 0 0 2

5. Transporter 1 Company Name: Tri-State Motor Transit Co. | 6. US EPA ID Number: MOD095038998

C. Illinois Transporter's ID: 1 5 1 3

D. (800) 723-8768 Transporter's Phone

7. Transporter 2 Company Name | 8. US EPA ID Number

E. Illinois Transporter's ID

F. ( ) Transporter's Phone

9. Designated Facility Name and Site Address: Westinghouse Hanford Co., 2355 Stevens Drive, Richland, WA 99352 | 10. US EPA ID Number: Central Waste Complex ATTN: Don Pyzel WA7890008967

G. Illinois Facility's ID: 1 9 5 3 0 0 5 5 1 2 8

H. Facility's Phone: (509) 373-5187

	11. US DOT Description (Including Proper Shipping Name, Hazard Class, and ID Number) HM	12. Containers No.	Type	13. Total Quantity	14. Unit Wt/Vol	I. Waste No.
GENERATOR a. X	Waste Radioactive Material LSA nos Radioactive Material UN2912 RQ(EPA EP Toxicity)	017	DM	009350	G	EPA HW Number XXF001 Authorization Number
b. X	Waste Radioactive Material LSA nos Radioactive Material UN2912 RQ(EPA EP Toxicity)	003	DM	001650	G	EPA HW Number XXF001 Authorization Number
c. X	Waste Radioactive Material LSA nos Radioactive Material UN2912 RQ(EPA EP Toxicity)	026	DM	014310	G	EPA HW Number XXF001 Authorization Number
d. X	Waste Radioactive Material LSA nos Radioactive Material UN2912 RQ(EPA EP Toxicity)	002	DM	001100	G	EPA HW Number XXF001 Authorization Number

J. Additional Descriptions for Materials Listed Above: Line A = F002 thru F005, D004 thru D011, D036, D040, D039, WT02, WC02, WP02
Line B = F002, F003, F005, D004 thru D010, D018, WT02, WC02
Line C = F002, F003, F005, D006 thru D010, D036, D039, WT02, WC02, F004
Line D = F002, F003, F005, D004 thru D011, D036, WT02, WC02

K. Handling Codes for Wastes Listed Above in Item # 14: G = Gallons Y = Cubic Yards

15. Special Handling Instructions and Additional Information

16. **GENERATOR'S CERTIFICATION:** I hereby declare that the contents of this consignment are fully and accurately described above by proper shipping name and are classified, packed, marked, and labeled, and are in all respects in proper condition for transport by highway according to applicable international and national government regulations.
If I am a large quantity generator, I certify that I have a program in place to reduce the volume and toxicity of waste generated to the degree I have determined to be economically practicable and that I have selected the practicable method of treatment, storage, or disposal currently available to me which minimizes the present and future threat to human health and the environment; OR, if I am a small quantity generator, I have made a good faith effort to minimize my waste generation and select the best waste management method that is available to me and that I can afford.

Printed/Typed Name: John Herman for ANL | Signature: John Herman | Date: Month 04 Day 26 Year 93

TRANSPORTER

17. Transporter 1 Acknowledgement of Receipt of Materials

Printed/Typed Name: James Elmer Jones | Signature: James Elmer Jones | Date: Month 04 Day 26 Year 93

18. Transporter 2 Acknowledgement of Receipt of Materials

Printed/Typed Name | Signature | Date: Month Day Year

FACILITY

19. Discrepancy Indication Space

20. Facility Owner or Operator: Certification of receipt of hazardous materials covered by this manifest except as noted in item 19.

Printed/Typed Name: Bruce A Rogers | Signature: Bruce A. Rogers | Date: Month 04 Day 29 Year 93

This Agency is authorized to require pursuant to Illinois Revised Statute 1989, Chapter 111 1/2, Section 1004 and 1021, that this information be submitted to the Agency. Failure to provide this information may result in a civil penalty against the owner or operator not to exceed $25,000 per day of violation. Falsification of this information may result in a fine up to $50,000 per day of violation and imprisonment up to 5 years. This form has been approved by the Forms Management Center

COPY 1. TSD MAIL TO GENERATOR

APPENDIX VI

STRAIGHT BILL OF LADING

ORIGINAL—NOT NEGOTIABLE

Shipper No. 169410

Carrier No. _____

Page 1 of 7 | Tri State Motor Transit (Name of carrier) (SCAC) | Date 4-26-

Any Gov't Rates or Discounts shall apply on this Shipment

On Collect on Delivery shipments, the letters COD must appear before consignee's name or as otherwise provided in Item 430, Sec. 1

TO: Consignee: WEstinghouse Hanford Corp

Street: 2355 Stevens Drive

City: Richland State: WA Zip Code: 99352

FROM: Shipper: ARGONNE NATIONAL LABORATORY For U. S. Dept. of Energy

Street: 9700 South Cass Avenue

City: Argonne State: IL Zip Code: 60439

24 hr. Emergency Contact Tel. No.: 708-252-6130

ATTN: R. Pedraza

~~Tri State Motor Transit~~ TRAILER # 448589

Vehicle Number: 670

No. of Units & Container Type	HM	BASIC DESCRIPTION Proper Shipping Name, Hazard Class Identification Number (UN or NA) per 172.101, 172.202, 172.203	TOTAL QUANTITY (Weight, Volume, Gallons, etc.)	WEIGHT (Subject to Correction)	RATE	CHARGES (For Carrier Use Only)
48 drums		Waste Radioactive Material LSA N.O.S.	343 cu. ft.	23,261		
		Radioactive Material				
		UN2912 RQ (EPA EP Toxicity)				
		Physical Description: Solid				
		Chemical Description: Solidified Sludge				
		Total Activity 149.9 mCi				
		Breakdown for Radionuclides and Activity				
		See Attached List				
			Shipments must be unloaded by consignee from the transport vechicle in which orginally load			
		Exclusive Use Radioactive Waste for disposal Driver to contact Joyce Demarest (509) 376-7768 24 Hours before delivery	Transportation thereunder is for the Government, and the actual transportation cost paid to the carrier(s) by the shipper or receiver is to be reimbursed by the Government.			

PLACARDS TENDERED: YES ☒ NO ☐

REMIT C.O.D. TO: ADDRESS

Note — Where the rate is dependent on value, shippers are required to state specifically in writing the agreed or declared value of the property.

The agreed or declared value of the property is hereby specifically stated by the shipper to be not exceeding

$ 40¢ per lb

I hereby declare that the contents of this consignment are fully and accurately described above by proper shipping name and are classified, packed, marked and labeled, and are in all respects in proper condition for transport by ☒ Rail ☒ Highway ☒ Water (DELETE NON-APPLICABLE MODE OF TRANSPORT) according to applicable international and national governmental regulations.

Andy Bracken Signature

COD Amt: $

Subject to Section 7 of the conditions, if this shipment is to be delivered to the consignee without recourse on the consignor, the consignor shall sign the following statement:

The carrier shall not make delivery of this shipment without payment of freight and all other lawful charges.

(Signature of Consignor)

COD FEE: PREPAID ☐ COLLECT ☐ $

TOTAL CHARGES: $

FREIGHT CHARGES: FREIGHT PREPAID (except when box at right is checked) ☐ Check box if charges are to be collected

RECEIVED subject to the classifications and lawfully filed tariffs in effect on the date of the issue of this Bill of Lading, the property described above in apparent good order except as noted (contents and condition of contents of packages unknown), marked consigned, and destined as indicated above which said carrier (the word carrier being understood throughout this contract as meaning any person or corporation in possession of the property under the contract) agrees to carry to its usual place of delivery at said destination, if on its route, otherwise to deliver to another carrier on the route to said destination. It is mutually agreed as to each carrier of all or any of said property over all or any portion of said route to destination and as to each party at any time interested in all or any said property, that every service to be performed hereunder shall be subject to all the bill of lading terms and conditions in the governing classification on the date of shipment.

Shipper hereby certifies that he is familiar with all the bill of lading terms and conditions in the governing classification and the said terms and conditions are hereby agreed to by the shipper and accepted for himself and his assigns.

SHIPPER: ARGONNE NATIONAL LABORATORY

PER: C. Bracken 4-26-93

CARRIER: Tri State Motor Transit

PER: X James Elmer Jones

DATE: 04-26-93

Permanent post-office address of shipper

PRINTED ON RECYCLED PAPER USING SOYBEAN INK SOY INK

STYLE F65 LABELMASTER, Div. of American Labelmark Co., Chicago, IL 60646 312/478-0500

LAND DISPOSAL RESTRICTION NOTICE

THE WASTES INDENTIFIED ON MANIFEST NUMBER 10001 AND BEARING THE EPA HAZARDOUS WASTE NUMBERS LISTED BELOW, ARE SUBJECT TO THE LAND DISPOSAL RESTRICTIONS OF 40 CFR PART 268.

THE WASTES DO NOT MEET THE TREATMENT STANDARDS SPECIFIED IN PART 268 SUBPART D, OR DO NOT MEET THE PROHIBITIONS SPECIFIED IN 268.32 OR RCRA SECTION 3004(d). THE TREATMENT METHODS OR PROHIBITION LEVELS APPLICABLE TO EACH WASTE ARE INDENTIFIED BELOW:

DRUM NO.	HAZ. WASTE NO.	TYPE	LEGEND NO.	CFR REFERENCE FOR TREATMENT STANDARD
1 - 17	D004-D011	NWW		40CFR268.41a TABLE CCWE
	F001	NWW	21	40CFR268.43a TABLE CCW
	F002	NWW	25	"
	F003	NWW	28	"
	F004	NWW	19	"
	F005	NWW	17,22	"
18-20	D004-D010	NWW		40CFR268.41a TABLE CCWE
	F001	NWW	16	40CFR268.43a TABLE CCW
	F002	NWW	21	"
	F003	NWW	1	"
	F005	NWW	17	"
21-46	D006-D010	NWW		40CFR268.41a TABLE CCWE
	F001	NWW	16	40CFR268.43a TABLE CCW
	F002	NWW	21	"
	F003	NWW	1	"
	F004	NWW	19	"
	F005	NWW	17	"
47,48	D004-D011	NWW		40CFR268.41a TABLE CCWE
	F001	NWW	16	40CFR268.43a TABLE CCW
	F002	NWW	16	"
	F003	NWW	1	"
	F005	NWW	2	"

LEGEND FOR TREATMENT STANDARDS

TABLE CCW-CONSTITUENT CONCENTRATION IN WASTES

	F001-F005 spent solvent	Waste Water Containing Spent Solvents (in mg/l)	+All other Spent Solvent Wastes (in mg/kg)
Legend #	Constituent Name		
1	Acetone	0.28	160
2	Benzene	0.070	3.7
3	n-Butyl alcohol	5.6	2.6
4	Carbon disulfide	0.014	NA*
5	Carbon tetrachloride	0.057	5.6
6	Chlorobenzene	0.057	5.7
7	Cresol (m- and p- isomers)	0.77	3.2
8	o-Cresol	0.11	5.6
9	Cyclohexanone	0.36	NA*
10	1,2-Dichlorobenzene	0.088	6.2
11	Ethyl acetate	0.34	33
12	Ethyl benzene	0.057	6.0
13	Ethyl ether	0.12	160
14	Isobutyl alcohol	5.6	170
15	Methanol	5.6	NA*
16	Methylene chloride	0.089*	33
17	Methyl ethyl ketone	0.28	36
18	Methyl isobutyl ketone	0.14	33
19	Nitrobenzene	0.068	14
20	Pyridine	0.014	16
21	Tetrachloroethylene	0.056	5.6
22	Toluene	0.08	28
23	1,1,1-Trichloroethane	0.054	5.6
24	1,1,2-Trichloroethane	0.030	7.6
25	Trichloroethylene	0.054	5.6
26	1,1,2-Trichloro-1,2,2,-trifluoroethane	0.057	28
27	Trichloromonofluoro-methane	0.02	33
28	Xylenes (total)	0.32	28

DATE PAGE 4 OF 7

TO WHOM IT MAY CONCERN,

THE 48 DRUM SHIPMENT OF MIXED WASTE TO HANFORD, #9304-10 CONTAINS THE FOLLOWING ISOTOPES IN LOW SPECIFIC ACTIVITY AMOUNTS:

Cs-137
Ba-137
Co-60
Ni-60m
Am-241
Sb-125
Te-125
Np-237
Na-22

DATE PAGE 5 OF 7

TO WHOM IT MAY CONCERN,

THE ACTIVITIES PER CONTAINER, FOR SHIPMENT #9304-10 OF MIXED WASTE TO HANFORD ARE AS FOLLOWS:

ALL UNITS IN MILLECURIES

1 -	4.0	mCi	41 -	0.5	mCi
2 -	4.0		42 -	0.4	
3 -	4.1		43 -	0.5	
4 -	4.2		44 -	0.4	
5 -	4.9		45 -	0.5	
6 -	4.8		46 -	0.4	
7 -	4.3		47 -	17.0	
8 -	4.5		48 -	23.0	
9 -	4.3				
10 -	5.0				
11 -	4.8				
12 -	4.5				
13 -	5.3				
14 -	4.8				
15 -	4.8				
16 -	5.0				
17 -	3.6				
18 -	6.4				
19 -	7.3				
20 -	5.6				
21 -	0.4				
22 -	0.5				
23 -	0.5				
24 -	0.4				
25 -	0.4				
26 -	0.4				
27 -	0.5				
28 -	0.4				
29 -	0.4				
30 -	0.5				
31 -	0.4				
32 -	0.4				
33 -	0.5				
34 -	0.4				
35 -	0.4				
36 -	0.4				
37 -	0.4				
38 -	0.4				
39 -	0.4				
40 -	0.4				

TOTAL = 149.9 mCi (Millicuries)

U.S DEPARTMENT OF ENERGY
INSTRUCTIONS REGARDING CONTROLS FOR RADIOACTIVE SHIPMENTS CONSIGNED AS EXCLUSIVE USE (SOLE USE OR FULL LOAD)

Conveyance No (s) 448589

Shipper's Shipment I. D. No. 169408 Date: 4-26-93

RESPONSIBILITY

These written instructions are provided to the carrier named on the shipping papers for the above referenced shipment and are to be maintained with the said shipping papers. It is the carrier's responsibility to ensure that these instructions are conveyed to its driver(s) and administrative personnel, as appropriate, for the duration of the movement to final destination.

INSTRUCTIONS

1. Maintain exclusive use of this vehicle for the duration of the movement. No other freight is to be loaded with this shipment except as directed by the consignor.

2. All loading or unloading of freight in this shipment shall only be done, or as directed, by the consignor or consignee.

3. The carrier is to move this shipment without delay, but in accordance with the legal statutes of transit jurisdictions.

4. Stops enroute are to be minimized to the extent practical and limited to accepted safe haven areas.

5. The carrier is to take positive steps enroute and during necessary stops to segregate this shipment from other freight, building, and personnel, so as to minimize potential exposures.

6. The carrier is to make peridoic inspection of equipment, load and placarding at appropriate intervals enroute to ensure maintenance of shipment safety controls.

7. To the maximum extent practical, the carrier, when movement is by highway, is to use interstate or limited access divided highways and avoid high density urban areas, especially where circumferential interstate highways are available to allow avoidance of travel through the highest populated portion of an urban.

SPECIAL HANDLING INSTRUCTIONS

1. If provided, by highway, the carrier driver is to maintain visual contact with escort(s).

2. Radiation surveys enroute will be made only with acceptable monitoring devices and the consignor or consignee will be notified that such monitoring has been done and by whom. Radiation surveys taken at the destination by authorized personnel of the consignee will be provided to the carrier on request or the carrier will be notified if there are contamination levels that would warrant taking the conveyance out of service.

3. The carrier is to take the appropriate emergency response actions should an accident or spillage occur enroute. The carrier will make notification as indicated on accompanying shipping papers in the event of a delay, accident, emergency enroute.

4. In the event that this is a Highway Route Controlled shipment per the shipping papers, the carrier is to comply with the requirement of DOT 49 CFR 177.825.

ARGONNE NATIONAL LABORATORY

9700 SOUTH CASS AVENUE, ARGONNE, ILLINOIS 60439

EMERGENCY RESPONSE

(708)252-6130 (ARGONNE FIRE DEPARTMENT)

GUIDE NO. 62

DATE: 4-26-93 **SHIPPING ORDER NO.** 169408

PROPER SHIPPING NAME: WASTE RADIOACTIVE MATERIAL LSA N.O.S

HAZARD CLASS 7 **I.D. NO.** UN 2912

RQ (EPA EP TOXICIT

POTENTIAL HAZARDS

HEALTH HAZARDS

Radioactive material; degree of hazard will vary from little to moderate, depending on type and quantity of radioactive material.
Many of these materials may not have radioactive materials labels.
Some radioactive materials cannot be detected by commonly available instruments.
Spilled radioactive materials usually will be visible if packaging fails.
Runoff from fire control or dilution water may cause pollution.

FIRE OR EXPLOSION

Some of these materials may burn, but none of them ignites readily.
Radioactivity does not change flammability or other properties of the materials.

EMERGENCY ACTION

Keep unnecessary people at least 150 feet upwind of spill; greater distances may be necessary for people downwind, or if advised by Radiation Authority.
Isolate hazard area and deny entry.
Response actions may be performed prior to any radiation measurements.
Positive pressure self-contained breathing apparatus (SCBA) and structural firefighters' protective clothing will provide limited protection.
Notify Radiation Authority of accident conditions.
Detain uninjured persons, isolate equipment with suspected contamination, and delay cleanup until instruction of Radiation Authority.
Call ANL Fire Department (708)252-6130 for EMERGENCY ASSISTANCE. If water pollution occurs, notify the appropriate authorities.

FIRE

Do not move damaged containers; move undamaged containers out of fire zone.
Small Fires: Dry chemical, CO2, water spray or regular foam.
Large Fires: Water spray, fog or regular foam.

SPILL OR LEAK

Do not touch damaged containers or spilled material.
Dike far ahead of spill to collect runoff water.
Cover powder spill with plastic sheet or tarp to minimize spreading.

FIRST AID

Use first aid treatment according to the nature of the injury.
If not affecting injury, remove and isolate suspected contaminated clothing and shoes; wrap victim in sheet or blanket before transporting.
If there is no injury, remove and isolate suspected contaminated clothing and shoes; assist person to shower with soap and water and notify Radiation Authority of action.
Advise medical personnel that victim may be contaminated with low-level radioactive material.

CHAPTER 13

Analysis and Treatment Applications

TREATMENT OF AQUEOUS MIXED WASTES CONTAINING RCRA METALS

H. No, D. G. Wygmans, D. B. Chamberlain, C. Conner, J. C. Hutter, C. Srinivasan, R. A. Leonard, L. Nunez, J. Sedlet, and G. F. Vandegrift

Argonne National Laboratory, Argonne, IL

ABSTRACT. A treatment process was developed for liquid radioactive mixed wastes containing hazardous metals and/or acids and bases. The process uses precipitation/pH adjustment with calcium hydroxide followed by precipitation with sodium sulfide. The resulting slurry is then filtered to remove the hazardous metal precipitates, and the resulting nonhazardous filtrate volume is reduced by evaporation. The performance of the process was determined on the laboratory scale; a design of the pilot-scale process was completed; and a process control strategy that uses on-line control of both pH and sulfide was developed. Results from the laboratory scale testing on various mixed wastes are reported.

INTRODUCTION

Mixed wastes (MW) contain both radioactive and hazardous materials. Mixed aqueous wastes containing α and/or β/γ activity along with various hazardous metals are commonly generated from nuclear research and development activities at Argonne National Laboratory. For these wastes to be acceptable for disposal at the Hanford site in Richland, WA, they must be solidified. As part of the Hanford acceptancy criteria, a plan must be in place to reduce the volume of MW generated; therefore, treatment should reduce the volume of the waste, neutralize the acid or base to non-corrosive levels, and reduce the toxicity of the hazardous metals by converting them to non-leachable salts. Removal of the Resource Conservation and Recovery Act (RCRA) metals (As, Ba, Pb, Cd, Cr, Ag, Se, Hg) from solution can be readily accomplished by precipitation (1,2). The metals are converted to an insoluble form and removed by filtration. The resulting filtrate can be classified as a low level waste (LLW) since the concentrations of the RCRA metals are lowered to levels below concern. Considerable volume reduction of the LLW liquid stream can be accomplished by evaporation. Although there are other metal removal methods, precipitation offers both simplicity and cost effectiveness.

A pilot-plant demonstration to remove ^{85}Sr, ^{137}Cs, Cd, Pb, U, Fe, Ca, benzene, and trichloroethylene from groundwater leachates was completed at Chalk River Laboratories (3). Since groundwater was being treated, the high water hardness required a modified lime-soda softening process (4,5) to remove the Ca and ^{85}Sr (both Ca and ^{85}Sr have a similar precipitation chemistry). Zeolite was necessary to recover the ^{85}Sr and ^{137}Cs, since the precipitation process cannot remove 100% of the dissolved ions (6). An earlier version of a similar lime-soda softening process was operated at Oak Ridge National Laboratory during 1957-1975; clay was used as the ion-exchange agent for ^{90}Sr and ^{137}Cs (6). Since 1975, the SPIX (Scavenging Precipitation Ion Exchange) process has been used (6). In this process, NaOH is added to precipitate $CaCO_3$ at pH 12. The initial precipitation process results in about 50% removal of the ^{90}Sr. In addition, ferrous sulfate (scavenging precipitate) and ion exchange are used to remove the remaining cesium and strontium. At the Savannah River Site, precipitation of iron and aluminum in a high nitrate salt waste at pH 7 is used to prevent fouling of downstream reverse-osmosis units, and ion exchange is used to remove radionuclides from LLW streams (6).

Complexing agents can interfere with precipitation processes (6). For these precipitation processes to function, the complexing agent must be destroyed by ozone, peroxide, chlorine, or other oxidizer. At Los Alamos National Laboratory, a ferric flocculation process gave poorer performance when complexing agents were present, and the combination magnesium hydroxide/ferric flocculation process was effective in the presence of complexants such as ethylene diamine tetra-acetic acid (EDTA) (6). Successful removal of RCRA metals from aqueous wastes containing complexants is very difficult. Only limited success has been reported. Fortunately, metal complexants are not commonly found in the wastes generated at Argonne. Aqueous toxic metal mixed wastes can be divided into three classes:

Class 1. Metals that can be removed by an alkaline sulfide precipitation. These are Cd, Cr(II, III), Hg(I, II), Pb(II), and Ag(I).

Class 2. Metals that require a simple pretreatment before they can be removed by the alkaline sulfide precipitation procedure. This class includes only Cr(VI), chromate or dichromate.

Class 3. Metals, oxidation states, or additional waste components that require special pretreatment and/or a different precipitation procedure than that for Class 1 metals. These include barium, arsenic, metals in solution with complexing agents, and rare oxidation states of some of the Class 1 metals.

Most of the waste at Argonne falls into Class 1. The combination hydroxide/sulfide precipitation process is robust enough to handle 95% of the liquid mixed wastes generated at Argonne. Unlike the typical radwaste treatment processes reported in the literature, the high removal of radioactivity from the liquid phase is not required. Thus, ion exchange polishing of the liquid phase is not required. Our process goal is to remove the RCRA metals at concentrations below regulatory limits so that the remaining liquid can be classified as a low level waste.

This article discusses the equipment used to complete this treatment, laboratory scale results for various types of mixed wastes, and a process control strategy.

EQUIPMENT DESCRIPTION FOR AN ALKALINE SULFIDE PRECIPITATION PROCESS

Treatment Equipment

The apparatus to treat Class 1 waste is shown in Fig. 1. The flocculation/precipitation tank has a 35.56-cm dia, is 68.58-cm high, and has a capacity of 21.7 L. Since the tank is made of polyethylene, it is resistant to both acids and bases. To promote flocculation, the 45° pitched blade turbine mixer impeller, (7.62-cm dia) was selected to attain a high pumping capacity at a low shear rate. It has a low solidity ratio (ratio of impeller projected area to the impeller swept area), which will allow a high flow to be induced in the tank. When operated at low speed (30 rpm), the impeller readily accomplishes both solids suspension and blending. Since the tank is not baffled, the impeller shaft was inserted at an angle of 15° off the center vertical axis of the tank. The impeller was rotated so that it pumped downward, the most efficient way to operate this impeller as a blending device (7). The tank has two feedback control loops: one for pH and the other for sulfide control.

The pH control loop consists of a pH electrode, proportional controller, analog-digital converter, and a diaphragm metering pump. The pH control loop activates the diaphragm metering pump to feed either acidic waste or the 0.1M stock nitric acid used for pH adjustment.

The sulfide control loop consists of a sulfide electrode and a reference electrode, proportional controller, analog-digital converter, and a diaphragm metering pump. The sulfide control loop activates the diaphragm metering pump to feed the 1.9M sodium sulfide solution. The tank has a high flow capacity pump, which

can be used to rapidly fill or empty the tank when the batch process is completed. Not shown in the figure is a temperature feedback loop, which can be used to shut down all the feed pumps in case the exothermic neutralization reactions causes an unacceptable high temperature (>45°C). This safety feature prevents mechanical failure of the polyethylene tank, which has a glass transition temperature near 110°C (8).

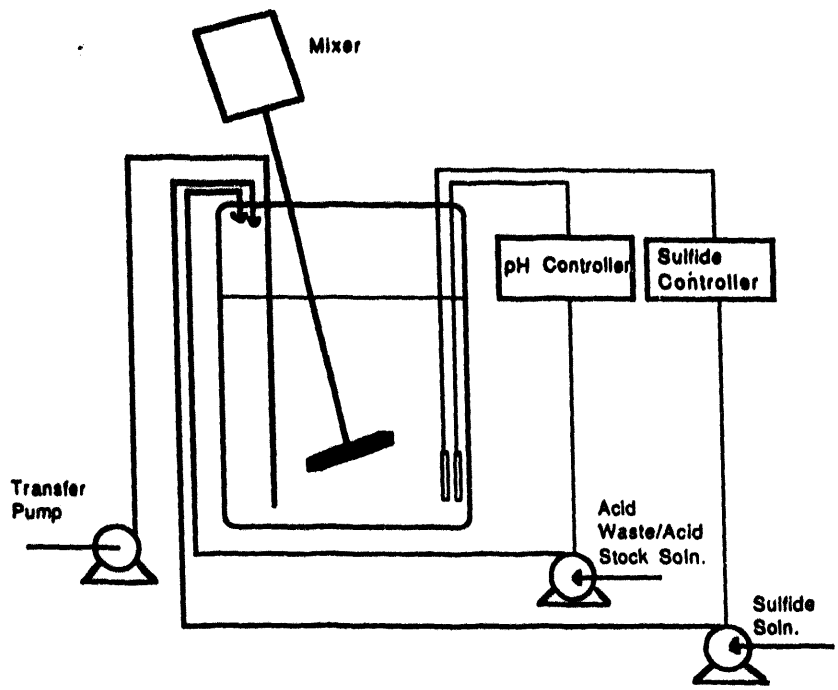

Figure 1. Alkaline sulfide flocculation/precipitation vessel.

Filtration Skid

A versatile filtration system, incorporating a number of modules, has been designed as shown in Fig. 2. The modular design allows the filtration scheme to be varied for research purposes and for treatment of a variety of influents. As seen in Fig. 2, most modules can either be included in or isolated from the flow scheme, as desired.

The bag filter, with filter elements in the 20-50 μm range, traps the bulk of the solids. A bag filter combines the advantages of high solids loading capacity and low disposable-cartridge volume, making this a valuable front-end filter. Plumbing connections in parallel with the bag filter will allow the later addition of a filter press or other pre-treatment option.

Two prefilters in parallel are included to protect the hollow fiber filter (HFF) from solids loading. One of the prefilter options is a disposable polypropylene mesh filter; the other is a sintered-metal filter with back-flushing capability. The metal element is easily flushed with liquid by reversing the flow through it. If the nature or size of the particles trapped by the filter makes flushing inefficient, the sintered-metal cartridge can be easily replaced by a disposable polypropylene cartridge. Both prefilters are in the 5-10 μm pore size range.

An open connection between the pre-filters and the HFF has been included to allow the addition of a carbon filter to adsorb dissolved organics from the aqueous stream. This addition may be necessary if streams containing dissolved organics are to be processed, since such organics would wet the pores of the HFF and plug it up. A carbon filter has not been included in the present design for two reasons: (1) present plans do not include processing aqueous streams containing dissolved organics, and (2) incorporation of two suitable-sized carbon filter would render the filter skid untransportable.

To adsorb volatile organic compounds (VOCs) dissolved in an aqueous liquid and reduce their concentrations from the ppm range to the ppb range, the superficial loading should be 2 gpm/ft2 (5). The depth of the filter will depend on the initial concentration of the VOCs and the desired life of the carbon bed.

The after filter, in parallel with the HFF will be used mainly as a backup for the HFF, for streams that cannot be run through the HFF (e.g., streams containing undissolved organics, which cannot be absorbed by the carbon filter). Pore sizes for the after filter will range from 1.0 to 0.1 μm.

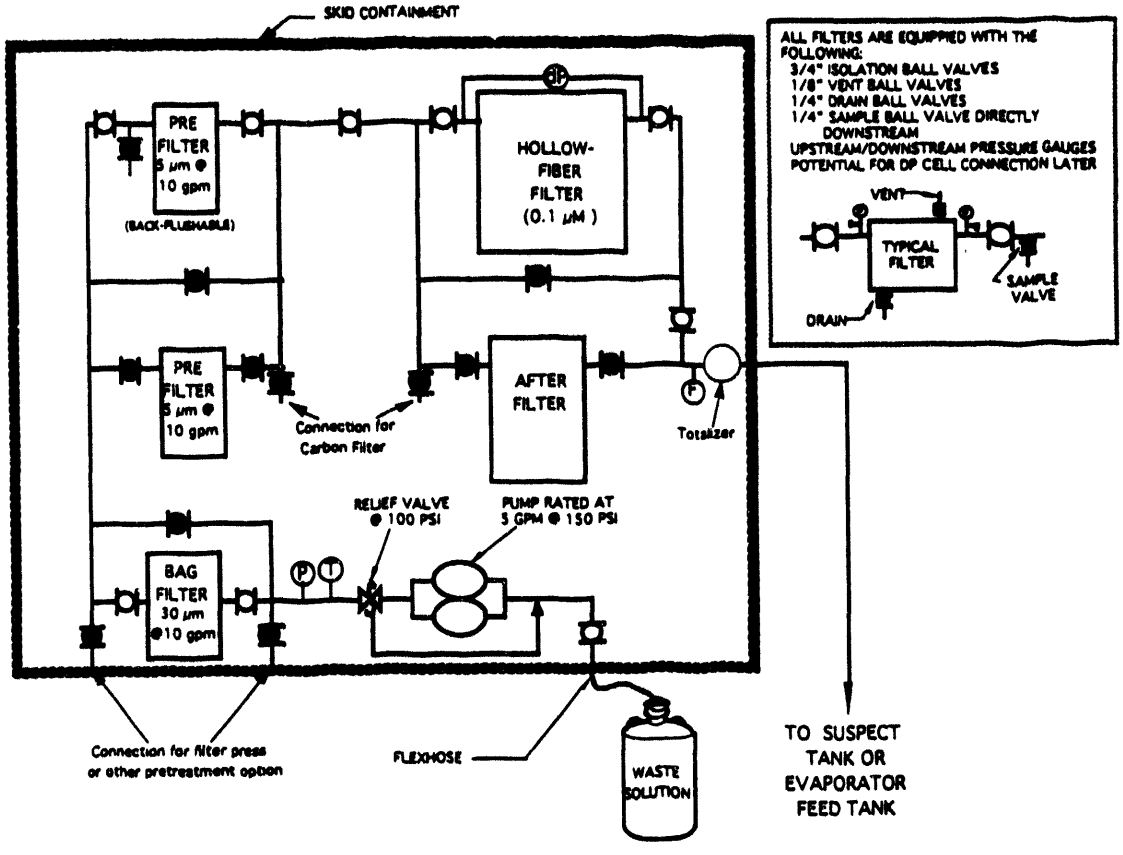

Figure 2. Schematic of filtration system.

The filter housings accept industry-wide standard cartridges, allowing the use of cartridges in a wide variety of pore sizes available from many manufacturers. Filter elements made with polypropylene will receive the most use. Each filter housing has pressure gauges upstream and downstream and a sampling valve directly

downstream to aid filtration studies. All housings are made of type 316 stainless steel and have pressure ratings of at least 150 psi (~1 MPa).

The feed will be pumped through the system by an electrically driven positive-displacement diaphragm pump. This variable-speed pump has a current draw of 25 A at 220 V and a rated output of 5 gpm (0.02 m^3/min) at 150 psi (~1 MPa). The diaphragm pump was chosen mainly because it has no seals and is self-priming. It also provides trouble-free pumping of slurries (up to 400 mm particle size) and the capability of running the pump dry without damage. The pump has a relief valve to ensure that the design pressure of 100 psi (0.7 MPa) is not exceeded. A pulsation dampener smoothes out the flow pulses generated by the pump, leaving a maximum pressure fluctuation of about ±1 psi (±7 kPa). A flex hose on the suction side of the pump allows for easy adjustment to a variety of feed-vessel sizes. The pump has a suction-lift capacity of at least 10 ft (3 m).

Total liquid holdup in the complete system will be about 14 gal (0.05 m^3). The maximum expected pressure drop across the system will be about 95 psi (0.7 MPa). This maximum accounts for plumbing losses as well as pressure drop across filters and will only be encountered when all filters, simultaneously, are in need of replacement or back-flushing.

CONTROL STRATEGY

pH Control

Control of pH for batch processes is a routine practice, and numerous commercial electrodes, controllers, and metering pumps are available. For batch processes, a simple proportional control is used since more complex PI or PID controllers are difficult to tune for systems with variable feeds. The offset that results from the proportional control does not affect the treatment results significantly. Acidic waste will be added to a $Ca(OH)_2$ slurry until the pH drops below 10.

Sulfide Control

Sulfide and pH controls are not independent of each other due to the chemical equilibria

$$S^{2-} + H^+ \text{ --> } HS^- \quad (1)$$

$$HS^- + H^+ \text{ --> } H_2S \quad (2)$$

The net reaction of Eqs. 1 and 2 is

$$S^{2-} + 2H^+ \text{ --> } H_2S \quad (3)$$

Thus, for every given value of pH, there is a fixed value for the concentration of S^{2-} as defined by Eq. 3.

On-line control of sulfide is not usually practiced, and sulfide is typically measured by grab sample analysis (9,10). The grab samples are mixed on a 50/50 basis with a basic sulfide anti-oxidant buffer solution (SAOB). The SAOB is made from sodium hydroxide, the metal complexant EDTA, and the antioxidant ascorbic acid (11). This procedure assures that the sulfide electrode (which only senses S^{2-}) reading correlates directly with the total free sulfide concentration. However, on-line monitoring of the total free sulfide concentration is possible if both the pH and sulfide electrode potential are known, and the sulfide electrode is inserted in a basic solution where the S^{2-}/S^0 redox is detectable by the electrode. In this situation, the free sulfide can be calculated from the chemical equilibrium. At pH 10 the free sulfide concentration of 1×10^{-4}M is detectable. This limit is more than adequate to maintain enough free sulfide

to ensure that the hazardous metals are below their RCRA concentration limits. This free sulfide concentration is far below the RCRA limit of 1.6 x 10^{-2}M (500 ppm). At pH 13.4 sulfide the detection limit of the electrode is 1 x 10^{-5}M, and the response of the electrode is linear up to 0.1M. Calibration curves which relate sulfide electrode potential to sulfide concentration at various pH levels are shown in Fig. 3.

To calibrate the sulfide electrode, standard solutions of sodium sulfide were prepared in the SAOB. Sulfide solutions were prepared by dissolving known amounts of $Na_2S \cdot 9H_2O$ in water. This material is hygroscopic, and the sulfide solution was standardized by titration against a lead nitrate solution. The end point for this titration was well defined.

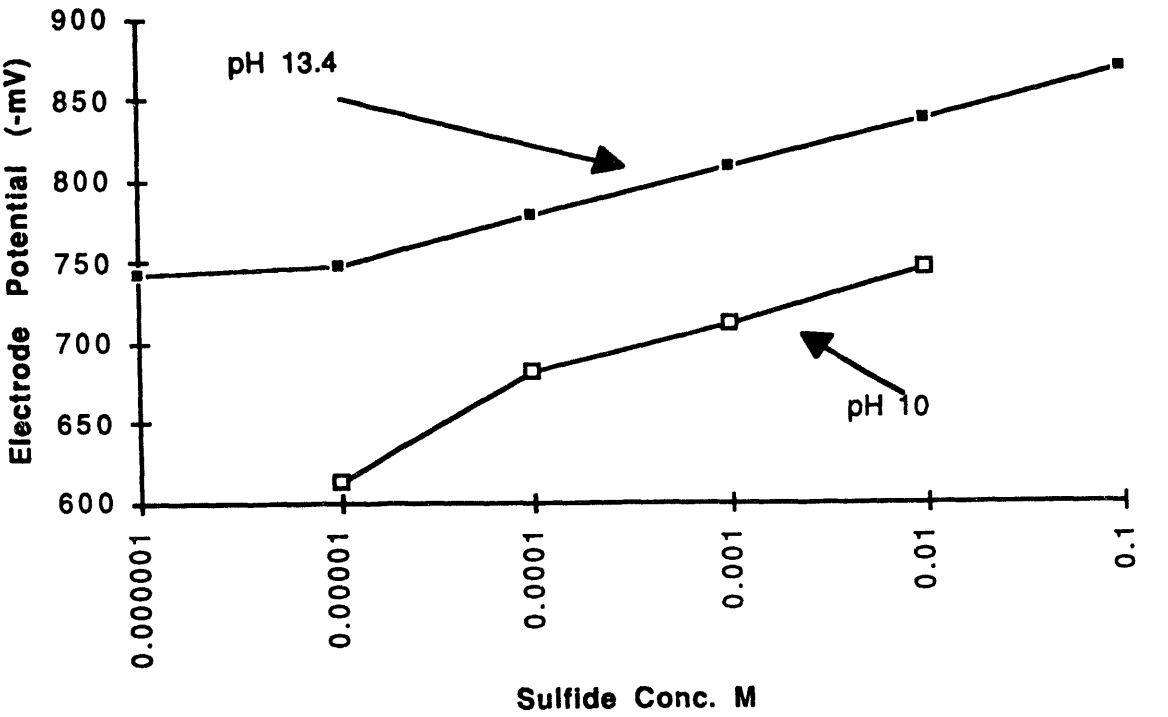

Figure 3. Calibration curves for sulfide electrode.

Operating Procedure

To flocculate and precipitate the RCRA metals in the mixed waste solutions, the acid waste stream will be added to a 10 wt% slurry of $Ca(OH)_2$, which neutralizes the acids and precipitates the metals as hydroxides. Metal removal will be completed by adding a sodium sulfide solution. The precipitated metal hydroxides are converted to sulfides. Process advantages are also realized by adding the acid to the $Ca(OH)_2$ slurry: (1) the $Ca(OH)_2$ can be prepared as a slurry directly in the treatment tank, (2) the pH of the treated waste will always be below the RCRA limit of 12.5, since the hydroxide slurry has pH 12.3 initially and any additional aliquot of acid waste will only reduce the pH. The waste acid addition will be stopped when a pH of 10 is achieved. Waste acid is metered by a diaphragm pump actuated by a proportional controller. Once a pH of 10 is achieved, the acid waste addition will be stopped, and the pH control loop will be inactivated. Next, a 1.9M sodium sulfide solution will be added until a total free sulfide concentration of 1-3 ppm is achieved. When sulfide is added to the waste solution, the pH of the solution rises, since sulfide converts the metal hydroxides to sulfides. The initial set point for the sulfide controller will be the millivolt

reading corresponding to a free sulfide concentration of 1-3 ppm at pH 10. Once this set point is reached, the pH will be remeasured, a new sulfide set point will be determined at this intermediate condition corresponding to a free sulfide concentration of 1-3 ppm at the measured pH, and the sulfide addition will continue until this updated set point is reached. Once this new sulfide end point is reached, the resulting pH should not be changed significantly, and the targeted free sulfide concentration will have been achieved. If the pH has increased above 12.5, a 0.1M HNO_3 solution will be metered into the waste to lower the pH to below 12.5. The pH control loop for this addition is the same one used for the waste acid addition.

LABORATORY SCALE TESTING OF RCRA METAL REMOVAL

The RCRA metal removal was tested on a laboratory scale to determine the dynamics and effectiveness of the proposed treatment process. The experiments were conducted in a 250 mL beaker agitated by a magnetic stirrer. Initially, a solution of 0.1M $Cd(NO_3)_2$, 0.1M $Pb(NO_3)_2$, and 0.1M $AgNO_3$ in 2M HCl was added to 50 mL of 10 wt % $Ca(OH)_2$ slurry until a pH of 10 was achieved. Upon addition of sodium sulfide, a black precipitate formed. This sulfide addition caused the pH to rise slightly, and the pH was adjusted back to 10 by the addition of more waste. The resulting slurry was passed through a 0.45 μm filter, and the filtrate was analyzed for the Cd, Pb, and Ag. The results of the experiments are shown in Table 1. Metal concentrations were determined by inductively coupled plasma/atomic emission spectroscopy (ICP-AES). The S^{2-} ions were used up for the precipitation of the RCRA metals and the precipitation of the Ca^{2+}. The OH^- was reacted stoichiometrically with the acid. The resulting solution could be maintained between the RCRA pH limits of 2 and 12.5 and under the sulfide limit of 500 ppm. As shown in the table, the metals were efficiently removed from the aqueous solution.

Table 1. Concentrations of Cd, Pb, and Ag in the filtrate following the alkaline sulfide precipitation procedure.

Metal	Waste (ppm)	Filtrate (ppm)	RCRA Limit (ppm)
Cd	11241	<0.05	1.0
Pb	20720	<0.5	5.0
Ag	10786	<0.05	5.0

TREATMENT OF DAVIES-GREY WASTE

Davies-Grey waste is one of the many types of mixed wastes generated at the Argonne site. Because it contains both radioactive and hazardous chemicals (chromium with pH<2), it is considered a mixed waste. The Davies-Grey method is used to quantitatively determine uranium. In this procedure, U(IV) is titrated against a standard solution of potassium dichromate in the presence of a catalyst. The aqueous waste is highly acidic (~3M phosphoric acid, with smaller amounts of nitric, sulfuric, and sulfamic acids) and contains iron, vanadium, molybdenum, and chromium in addition to uranium.

Batch tests on this waste were completed to develop procedures that will treat and dispose of this mixed waste. To treat this waste, the acid is neutralized by the addition of alkali, and at the same time the chromium is precipitated as insoluble chromium hydroxide. (No sulfide addition is required.) The precipitate can be separated by filtration and disposed of as a solid mixed waste. The filtrate in the pH range of 7-10 is a low level radioactive waste since it contains uranium. It can be concentrated by evaporation and disposed of at a LLW disposal site. It is possible that the uranium in the waste may also

be precipitated to a significant extent along with the chromium, leaving a liquid stream that is suitable for direct disposal into the drain at Argonne.

The oxidation states of chromium, iron, and uranium in the waste solutions are expected to be Cr(III), Fe(III), and U(IV). A small amount of Cr(VI) may coexist in these solutions, since small quantities of this component (potassium dichromate solution) were mixed with the waste.

The neutralization and precipitation experiments with Davies-Grey waste solutions were done by titrating the waste solution in a burette against a known quantity of either a 10 wt % calcium hydroxide solution or a concentrated (~10 M) sodium hydroxide solution in a beaker. The titrations were terminated in the pH range of 7 to 10. To test the completeness of chromium precipitation in solutions, where it exists in both the III and IV oxidation states, additional experiments were done with solutions to which measured amounts of potassium dichromate were added. At the end of the titrations, the solutions were passed through 0.65 μm filter. The original waste and the resulting filtrates were analyzed for chromium, iron, molybdenum, vanadium, and uranium by ICP-AES. The results of the analysis are given in Table 2.

Table 2. pH and concentrations of Cr, Fe, Mo, V, and U (all in ppm) in the Davies-Grey waste solution and treated filtrates.

Sample	pH	Cr	Fe	Mo	V	U
A. Davies-Grey waste	<1	21	1200	83	69	90
B. Davies-Grey waste w/potassium dichromate	<1	39	1200	83	69	90
$Ca(OH)_2$ treatment, waste A[a]	10.0	0.12	0.023	1.4	0.007	<1
$Ca(OH)_2$ treatment, waste A[a]	6.9	0.16	0.035	1.1	0.030	<1
$Ca(OH)_2$ treatment, waste B[a]	10.2	0.12	0.032	0.24	0.017	<1
NaOH treatment, waste A[b]	10.0	2.3	59	19	14	20
NaOH treatment, waste A[b]	6.9	1.6	50	19	14	19
NaOH treatment, waste B[b]	10.0	2.4	44	13	10	18

[a] $Ca_3(PO_4)_2$ sludge is formed.
[b] $NaPO_4$ sludge does not form due to the high solubility of the sodium form of the neutralization product.

As shown in Table 2, the removal of chromium and uranium by precipitation is more effective when calcium hydroxide is used. Since the Davies-Grey waste was rich in phosphoric acid, a substantial amount of calcium phosphate sludge formed when calcium hydroxide used. In the sodium hydroxide experiments, the sodium phosphate remained in solution. Furthermore, the concentrated solutions of sodium hydroxide contained dissolved carbonate ions, which kept the uranium in solution and thus impeded effective uranium removal. Chromium(VI) must have been removed from the solution by either co-precipitation or adsorption onto the flock; it should not precipitate as a hydroxide in the +6 oxidation state. Thus, reduction of Cr(VI) may not be required to meet the RCRA concentration limits for this waste.

ALTERNATIVE TREATMENT PROCEDURES FOR COMPLEX WASTES

The alkaline sulfide precipitation procedure discussed above will not treat all the possible mixed waste compositions. As discussed in the introduction, the wastes can be divided into three classes. Class 1 waste can be treated by the alkaline sulfide precipitation process, as discussed. Class 2 and 3 waste treatments require modified procedures. Waste solutions that are basic and contain Cr(VI), As, and Ba, or that posses unusual oxidation states of the metals must be treated by modified procedures.

Basic Wastes

In the absence of complexing agents, the only RCRA metals that can be present in basic solutions are Ba, Cr(VI), and As. If the solution is classified as a RCRA waste only because its pH is >12.5, it can be neutralized with 8M nitric acid by a procedure similar to that described above; however, the waste starts off in the flocculation tank (instead of a calcium hydroxide slurry), and the acid stock solution is added to the waste.

Chromium(VI)

Chromium (VI) exists as CrO_4^- (chromate) or $Cr_2O_7^{2-}$ (dichromate) in aqueous solution and must be reduced to Cr(III) in order to precipitate as the hydroxide. (The co-precipitation or adsorption of Cr(VI) in the Davies-Grey waste was an unusual case and cannot, in general, be expected to occur.) The reduction of Cr(VI) must be done under acidic conditions. If the solution is not acidic, the pH should be adjusted to 1 by the addition of 8M nitric acid. A 30 wt % solution of hydrogen peroxide can be added to the waste solution until the color changes from yellow to blue-green, which is the color of Cr(III). This change can also be monitored by measuring the oxidation-reduction potential. Once the Cr(VI) is reduced to Cr(III), the waste can be neutralized with a calcium hydroxide slurry until the pH is 7-10. At pH>10, the $Cr(OH)_3$ will begin to redissolve.

Arsenic

Arsenic(III) and (V) exist as H_3AsO_3 and H_3AsO_4 in acidic aqueous solutions and as salts of these acids in basic solutions. Both oxidation states can be precipitated as sulfides under acidic conditions. If the solution is not acidic, 8M nitric acid should be added to adjust the pH to 1. Then saturated Na_2S solution can be added until the free sulfide concentration is 50 ppm. During the sulfide addition, the pH must be monitored and kept near 1 by the addition of more nitric acid. When the free sulfide and temperature stabilize, the slurry can be filtered. In this situation, free sulfide cannot be measured on-line but must be measured by grab samples. After filtration, the filtrate must be treated as a corrosive waste, i.e., base added to increase the pH.

As an alternative, ferric hydroxide co-precipitation can be used when trace amounts of arsenic are present. For this process, 1M $Fe(NO_3)_3$ solution should be added to the waste to obtain a ferric ion concentration of 2 g/L, then the 10 wt % $Ca(OH)_2$ slurry can be added to adjust the pH to 7 to precipitate $Fe(OH)_3$ and the arsenic.

Arsenazo dyes are organic compounds containing As(V). They can be destroyed by oxidizing agents (H_2O_2, Cl_2, O_3) or strong reducing agents, such as Ti(III), $Na_2S_2O_3$ (12). Once the As(V) is released, the above treatment for arsenic precipitation can be used.

Barium

Barium(II) will not precipitate using the alkaline sulfide procedure. Waste solutions containing Ba(II) can be adjusted to a pH of 9 with saturated Na_2CO_3 to precipitate $BaCO_3$; Na_2CO_4 can also be used to precipitate Ba(II).

Rare Oxidation States of the Toxic Metals

Examples of the rare oxidation states of the RCRA metals are Pb(IV), and Se(VI). Waste solutions containing these species will be treated on a case-by-case basis and may have to be oxidized or reduced to be treated by the alkaline sulfide process.

CONCLUSIONS

An alkaline sulfide precipitation process was adapted for use in treating aqueous mixed wastes containing RCRA metals. A control strategy was developed to achieve the treatment goals of pH 10 and free sulfide of 1-3 ppm. Since both pH and sulfide concentrations are interacting due to chemical equilibria, precise control is possible by following a batch step-wise treatment procedure. The monitoring of the sulfide concentration can be accomplished using a sulfide ion selective electrode, a pH electrode, and calibration curves. Batch testing demonstrated the treatment chemistry and control strategy for several different kinds of mixed wastes.

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THE IMPORTANCE OF BENCH-SCALE TREATABILITY STUDIES IN PLANNING FOR MIXED WASTE SITE REMEDIATIONS

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ABSTRACT. Bench-scale treatability studies are fairly routinely carried out as part of the overall process of remediating a mixed waste site. The typical treatment processes involved include stabilization, thermal desorption, drying, soil washing, biotreatment and dechlorination. These studies are normally used to confirm the general applicability of a specific treatment technology to a specific remediation project and to determine whether or not the treatment technology will meet the cleanup standards for the project. They also allow selection of operational parameters and reagents to be used for the actual remediation. Often the measurements and analyses carried out on the sample provided for the study provide the most complete characterization of the waste obtained throughout the remediation process. Such a characterization can alter the course of the project, up to and including causing a change in the treatment technology of choice. Our actual experience in carrying out several treatability studies is described. In each case, the characterization results or the treatability study results were not "as expected", with the result that the treatability study had a significant impact on the overall project. It is generally assumed that the treatability study will predict the performance of the full-scale treatment system. For one thermal desorption treatability study a careful attempt was made to obtain a comparison of bench scale and full scale performance, with favorable results obtained.

INTRODUCTION

A bench-scale treatability study is an important facet of the overall strategic plan for remediation of a mixed waste site (1,2,3). Such tests are relatively simple and straight forward to carry out, and the U.S. Environmental Protection Agenct (EPA) has issued guidelines for conducting such studies (4). The sample sizes required are small, normally less than 30 kg, and costs are moderate. Studies can be carried out on a wide variety of remediation or treatment technologies including stabilization, thermal desorption, drying, soil washing, wastewater treatment, bioremediation, dechlorination and tarry waste treatment. Although treatability tests are a fairly routine practice carried out by companies in the remediation business, the utility of information provided by such tests is often not fully appreciated. This paper describes the importance and utility of bench-scale treatability studies in the remediation of mixed waste sites. A comparison of full scale and treatability study results for a thermal desorption process is also given.

INFORMATION GAINED FROM TREATABILITY STUDIES

Pre-treatability study sample characterization is generally the first step of the treatability study process. At the initial phase of the study, careful measurements are made of contaminant levels, chemical characteristics and physical properties of the waste matrix. Often, this is the first solid information of this type available for the waste. This is especially the case for non-Resource Conservation and Recovery Act (RCRA) type analyses such as water content, ash content, organic carbon, bulk density, viscosity, particle size distribution,

etc. Although not a concern from a regulatory standpoint, this type of analytical data is essential in facilitating evaluation of various remedial approaches. In addition, it is often discovered in the pre-treatability study sample characterization that concentrations of target constituents in the treatability samples are often much higher or lower than expected.

Preliminary screening of treatment variables (both operational parameters and reagents) is another important function of bench-scale treatability testing. These tests most often involve performing a large number of relatively simple, comparative treatment technology simulations, to assess the significance of treatment variables such as reagent type, reagent concentration, reaction time, reaction temperature, etc. For instance, many versions of soil washing are available, some selective for removal of organics and some selective for removal of heavy metals and radionuclides. Bench-scale testing is almost essential for the proper selection of wash chemical reagents and optimization of reagent dosage. The same is true for stabilization reagent selection and chemical conditioner selection for dewatering operations.

Another application of treatability testing is to demonstrate that a treatment system, typically selected from evaluation of treatability screening results, will reliably achieve performance criteria. This type of treatability testing is confirmatory in nature and should generally involve replicate runs to prove statistical significance in being able to meet the performance criteria. In those cases where the waste to be processed at the site is heterogeneous in nature, testing is also recommended at this stage (or earlier) to determine the sensitivity of the treatment process to changes in the feed waste composition. The matter of variability of feed waste is an often overlooked point but has proven to be a very significant (often the most significant) consideration for the field application.

In some cases, the remediation will be carried out using relatively sophisticated technology, often with several unit operations of a nature similar to those used in minerals processing or chemicals manufacture or separations. Examples are thermal desorption and soil washing. In these cases, the bench scale equipment used should be, to the greatest extent possible, a scale down of the proposed full scale plant, as recommended by Trambouze (5). The principles involved are not precisely defined, and considerable judgement is involved in achieving a proper and representative scale-down. See Robbins (6) for an excellent discussion of this subject. The type of instrumentation employed for the bench scale system can be important; see Kaufman (7). Materials of construction and size of equipment are also key considerations; see Vilbrandt and Dryden (8) and Corpstein (9).

SELECTED EXPERIENCES

We have performed a number of mixed waste remedial treatability studies over the past few years. These have involved stabilization, soilwashing, thermal desorption, distillation, ion exchange and dewatering technology applications. Some selected experiences which demonstrate the usefulness of treatability studies in the mixed waste remedial process will be discussed.

The Importance of Pre-Treatability Study Sample Characterization

The matter of properly characterizing samples prior to performing treatability studies is quite often sacrificed due to tight project schedules. For instance, we were once trying to separate radium from a drummed waste that reportedly contained methylene chloride and methanol. This was a "fast-track" project where our client could not allow time on the project schedule to perform and evaluate the preliminary characterization results before beginning the treatability study. Mid way through the study, which involved distillation and resin adsorption process simulations, the characterization results became available. It was discovered that absolutely no detectable methylene chloride or methanol could be found in the waste. The treatability study was canceled since the mixed waste issue was no longer of concern for this wastestream.

Another project involved the thermal desorption of mercury from a remediation site soil also contaminated with radionuclides. The treatment goal was to produce a treated product that was in compliance with the Toxicity Characteristic Leaching Procedure (TCLP) criteria for mercury. Since the allotted project schedule was short and it was known that the untreated material contained high levels of mercury (3,000 ppm), it was determined by our customer to perform the thermal desorption treatability simulations prior to receipt of preliminary analytical characterization results. The results of before and after treatment analyses are shown in Table 1. As can be seen by these data, the untreated material was in compliance with the TCLP mercury criteria. The sample provided for study was a "worst case" material and, thus, there was considerable question regarding the need to treat the material at all to meet the site treatment objective.

Table 1

	Untreated Soil	Thermally Treated Soil	Treatment Objective
Tot. Hg. (ppm)	2,770	3.1	N/A
TCLP Hg (ppm)	0.14	<0.0003	0.2

Another actual case study that illustrates the importance of obtaining a complete raw sample analytical characterization prior to performing treatability studies involves a chemical dechlorination project that we recently performed. The objective, here, was to dechlorinate polychlorinated biphenyls (PCB) in a radioactive sludge/liquid sample collected from a retention tank. The characterization information associated with the first sample supplied to our laboratory for treatability testing indicated no detectable concentration of PCBs. Another sample was provided which did contain detectable (albeit lower than expected) PCB concentrations. However, it was also determined by characterization analysis that a significant quantity of water was present in the sample to cause quenching of the dechlorination reaction. For the application of the treatment technology to be effective, a preliminary drying operation was determined to be necessary.

The Need to Assess the Impact of Treatment Variable Adjustment

Bench-scale treatability studies are often indispensible in affording an opportunity to determine which treatment reagents/dosages and operating conditions perform best. Simple but often important variables, such as order of arrangement of unit operations, can also be optimized. More often than the design engineers will admit, treatability studies have been a valuable 'early warning' announcing that assumed levels of treatment could not be achieved without significant system modifications.

A number of stabilization studies have been performed upon mixed waste samples in our laboratories. One project, in particular, involved the co-stabilization of radionuclides, heavy metals and nitrate. Successful cement-based or lime stabilization formulas were found to fix the radionuclides and heavy metals. However, nitrate could not be stabilized by such formulations without producing unacceptable volumetric increase. Therefore, nitrate had to be purged from the waste prior to stabilization with the rinsewater then treated in a subsequent operation. It was discovered, however, that lime stabilization had a negative impact upon the ability to rinse nitrate from the sludge. This is shown in Table 2.

Another stabilization study involved a soil contaminated with radionuclides and low concentrations of volatile organics. Significant planning and precautions were considered for this study to minimize and/or account for the loss of volatile organics in the handling and processing of the samples. However, it was observed during the bench-scale testing that mixing of the stabilizing agents with this particular site soil was extremely difficult. In the project report, the handling of the sample and concern over possible volatile

organic losses were greatly stressed by the lab staff. The matter of the mixing difficulty was not given much attention and, therefore, was not properly flagged to the project team that performed the field demonstration. This difficulty in mixing the reagents eventually became a very significant concern in the field causing modifications to be made to both equipment and procedures.

Use of bench-scale testing to optimize treatment variables was proved essential in enabling us to apply a soil washing technology to a site contaminated with "heavy" organics (greases, oils) and radionuclides (plutonium and americium). Based upon the best available information obtained from vendor sources and our own experience with similar applications, our initial bench testing indicated that we could only achieve radionuclide removals of 35 to 45%. This was far short of the goal of near 90%. The operational parameters that were studied included reaction time, pH, chelant concentration, complexing agent concentration, oxidant concentration, surfactant concentration, and temperature. Table 3 summarizes the results of these tests. With the optimization of the aforementioned operational parameters, we were able to demonstrate that the desired removal efficiencies could be achieved in the bench test, however, to achieve such removals, additional reagents and a heating process had to be incorporated into the treatment process originally envisioned. This technology application is currently being tested on a pilot-scale.

Table 2

Effectiveness of Stabilization/Filtration Rinsing Treatment

Treatment	Waste : Stabilizer Ratio	Rinse Rate (Chamber Volume)	TCLP U (ppm)	TCLP NO_3 (ppm)
Performance Goal			0.14	310
No treatment	N/A	N/A	40	800
Cement Based Formulation	1:1	0.5*	<0.01	70
	2:1	2	<0.01	130
	3:1	3	<0.01	---
	6:1	4	0.2	5
Hydrated Lime Formulation	3.7:1	0.5*	<0.6	400
	5:1	2	NR	490
	5:1	5	NR	500
	7.5:1	1	<0.2	NR

NR - Not Run
* - Indicates a displacement rinse

Determining the Sensitivity of the Process to Waste Non-Homogeneity

One often overlooked aspect of performing treatability studies is the ability of the recommended process to perform under variable feed conditions. Such variations may include concentration of target constituents, concentration non-target constituents (water, non-regulated substances) and changes in the waste matrix (sediment vs. soil, gravel vs. clay, etc.). Consideration must be given concerning how to predict the impact of process performance based upon feed materials variation that will actually be encountered in the field. On a recent project, our laboratory received six drums of "representative" process waste that was collected from the remedial site. Analysis of these drums indicated a five-fold concentration variation among the drums for one of the target constituents. Our studies were then designed to demonstrate process effectiveness for the target constituents over this concentration range. Another factor to consider is the importance of the treatability sample(s) being representative of actual conditions at the site. This matter is often overlooked. We once performed a study involving a drum site. A reportedly representative sample consisting of approximately 100 subsamples from 100 of several thousand drums was provided to us. We meticulously recorded observations on each of these containers, proportioned them into a composite sample and performed our treatability studies. The project was scaled up and sent to the field. In the field, the solids content of the process feed was determined to be approximately 25% versus the 45 to 50% solids content of the treatability sample. In that this technology was a drying system, the greater than anticipated water content was not compatible with the designed feed system nor with the projected treatment economics.

Scale-up and Prediction of Full-scale Performance

It is generally assumed that the treatability study will predict the performance of the full-scale treatment system to some extent. However, one must consider the design of the treatability study in the context of scale-up. In the very early stages of such studies, proof-of-concept testing performed with relatively common laboratory apparatus will often provide the required information. Once the proof-of-concept is established, however, there are cases where scale-up must be confirmed with prototypes to study system dynamics and interactions.

We performed a bench-scale thermal desorption study upon a mixed waste to effect separation of KO11 and KO13 organics from sludge which also contained natural uranium. Screening study results (using a muffle furnace operated under a nitrogen blanket) indicated that the degree of desired treatment could be achieved for the target constituents. However, in treatability testing using a prototype system, an applications difficulty was discovered. It was determined that significant entrainment of uranium fines in the off-gases would cause subsequent accumulation of radioactive materials in the gas scrubber sludge. Further work is still being performed to address this problem prior to construction.

It is important to obtain feedback on how well treatability test simulations predict performance of the full-scale system. The following is a case history where a careful attempt was made to obtain this comparison.

The X*TRAX® process is a thermal desorption process designed to remove organic contaminants from soils, sludges and other solid materials. An externally-fired rotary dryer is used to volatilize the water and organic contaminants into an inert carrier gas stream. The processed solids are then cooled with treated condensed water to eliminate dusting. The solids are ready to be placed and compacted in their original location. The organic contaminants and water vapor driven from the solids are transported out of the dryer by an inert nitrogen carrier gas. The carrier gas flows through a duct to the gas treatment system, where organic vapors, water vapors, and dust particles are removed and recovered from the gas. The gas first passes through a high-energy scrubber. The gas then passes through two condensers in series, where it is cooled to less than 40 degrees Fahrenheit. Most of the carrier gas is reheated and recycled to the dryer. Approximately 5 to 10 percent of the gas is cleaned by passing it through a particulate filter and a carbon adsorption system before it is discharged to the atmosphere.

Table 3

Optimization of a Soil Washing Process to Remove Plutonium and Americium

Test Set	Description	Percent Removal Based Upon Gross Alpha/Beta Results
1	Operational parameters set based upon best engineering judgement	35-45
2	Adjustments made to pH surfactant and complexing agent concentration	55-65
3	Adjustments made to reaction temperature	up to 80
4	Operational parameters optimized based upon results of test sets 1-4 (pH=9; surfactant @ 2%; temp. @ 50° C; chelant @ .07 M; complexing agent @ 0.5 M).	86

The process has been scaled up from a "bench"scale, actually a small, 2-4 lb/hr pilot scale, to a commercial-scale system with a 130 - 150 ton/day capacity. The full scale system is now in operation at the ReSolve Superfund site in North Dartmouth, MA, where it is being used to treat 35,000 tons of PCB-contaminated soil.

In May of 1992 the EPA conducted a Superfund Innovative Technology Evaluation (SITE) demonstration at the ReSolve site. The SITE technology demonstration was conducted early in the ReSolve site remediation on May 19 and 20, 1992. Soil treated during the demonstration contained PCBs at concentrations of approximately 150 to 350 parts per million. The demonstration collected performance and cost data during three identical 6 hr test runs to evaluate the effectiveness of the X*TRAX system. The treated soil was analyzed using both SW-846 Methods 8080 and 680. All sixteen soil samples taken where found to contain less than 1.0 ppm PCB using either analysis method. No evidence of dioxin formation was found, and no PCBs were detected in the unit's air emission.

We routinely conduct treatability studies for the X*TRAX process, using the small, 2 - 4 lb/hr pilot unit. Early treatability studies on two samples of soil from the ReSolve site had provided guidance for the proposal which led to the award of the contract to our company. After the SITE demonstration at ReSolve, however, it was decided to conduct yet another treatability study on soil from the site, this time using a sample of the actual feedstock used during the SITE demonstration. This would allow us to determine how accurately our bench scale studies predict the performance of the full scale system.

During November of 1992, a sample of soil from the feed pile used during the full scale ReSolve demonstration was processed through the small pilot X*TRAX unit, using our standard treatability procedures. During the laboratory testing, cylinder shell temperatures were selected to span the range of solids temperature measured during the full scale testing. Comparing the lab results with the full scale operation during the SITE demonstration produced almost identical results.

The average PCB concentration in the feed during the full scale test period was 227 ppm (64-314 ppm). The pilot plant sample contained 293 ppm of PCB. A comparison of the treated soil from both the small pilot and full scale X*TRAX is presented in Table 4 as a function of solids temperature.

Solids temperature is known to be a key variable in the process. Table 4 shows PCB concentration in the treated soil as a function of solids temperature at the discharge of the kiln. The data point from the commercial unit is seen to be consistent with the results from the pilot scale. Based on there results, we will continue to use the small pilot unit to predict the performance of the full scale system.

Table 4. Comparison of results, pilot and full scale.

Solids Temp (°F)	Treated Soil PCB Concentration (ppm)	
	Full Scale	Small Pilot Scale
625	-	1.7
695	-	0.09
735	0.80(1)	-
770	-	< 0.5

(1)Average of 1.7 datapoints. Concentration for BDL results assumed to be 50% of detection level.

CONCLUSION

These bench-scale studies were found to be of strategic importance in the development of the subsequent field remedial programs. Quite often, the most significant findings have been unexpected and not necessarily directly related to the application of the technology. Proper characterization of the samples prior to implementing the treatability program is essential to the success of the program. This characterization should focus not only on the regulated constituents but also on those other constituents or characteristics that could impact treatment performance. Once quantified, the presence/absence or degree of these constituents/characteristics should be used to assess the need for more or fewer processing steps.

Bench-scale treatability studies are also an important tool to assess the impact of adjusting both reagent dosage and operational parameters. Quite often, such adjustments can not be pre-determined. The number of treatment variables are often so numerous that it is difficult to engineer the desired degree of flexibility into the system without guidance provided by treatability studies.

Assessing the sensitivity of the treatment process to potential waste stream variability is also an important function of the bench-scale treatability study. Careful consideration must be made concerning how to assess the flexibility of the selected process to meet performance criteria in spite of waste stream variations. Collection of representative waste samples that are either worst-case (if such a determination can be made) or indicative of the expected range of wastestream variability is vital to the successful incorporation of treatability data into the remedial design process.

It also important to consider the ability to scale-up the technology from the bench test to the field application. This scale-up consideration should be a component of the treatability test program design and, if determined to be a significant concern, should be confirmed through the use of prototype demonstrations which are capable of processing sufficient quantities of material.

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CHARACTERIZATION OF RADIOACTIVE WASTES: TCLP AND MICROWAVE DIGESTION OF INORGANIC PROCESS SLUDGE, PYROCHEMICAL SALTS, AND ORGANIC RESINS

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ABSTRACT. A modified SW-846 Method 3051 microwave leach procedure for digestion of transuranic (TRU) waste was developed using surrogates for pyrochemical salt and organic resin waste. The modified procedure uses an aqua regia acid matrix and heating profiles that vary depending on the matrix. For these surrogates adequate spike recoveries were obtained for the Resource Conservation and Recovery Act (RCRA) elements Ag, As, Ba, Be, Cd, Cr, Ni, Pb, and Se. TRU inorganic process sludge was analyzed for RCRA metals after Toxicity Characteristic Leaching Procedure (TCLP) extraction and microwave HNO_3 acid digestion. The TCLP results show that analyte concentrations and spike recoveries for a 200mL extractor (10g sample) are within experimental error of those obtained with the 2L extractor (100g sample). Comparison of the TCLP results with those from Method 3051 digestion of the sludge (0.5g samples) suggests that the microwave method has potential as a screening technique for the analysis of mixed waste samples. A significant advantage of the microwave leach procedures is a minimum 10-fold reduction of waste produced.

INTRODUCTION

The characterization of a range of mixed waste is a problem facing many of the facilities throughout the U.S. Department of Energy complex. The wastes vary greatly in terms of matrix and radiological activity. We have been investigating the analysis for Resource Conservation and Recovery Act (RCRA) metals in three wastes: inorganic process sludge, pyrochemical salts, and organic resins. The activity of these wastes is as low as 600dpm for one of the inorganic sludges and may be greater than 2.22×10^{11} dpm (100mCi) for the pyrochemical salts. The primary radioactivity in these samples is due to the emission of alpha particles.

The direct application of U.S. Environmental Protection Agency (EPA) analytical methods to the determination of hazardous analytes in transuranic (TRU) waste has several drawbacks including waste minimization and personnel exposure issues. We have approached these problems by applying EPA SW-846 methods including Method 1311 (Toxicity Characteristic Leaching Procedure, TCLP) and Method 3051 (HNO_3 microwave digestion) (1-3) and comparing the results obtained using these sample preparation methods. In addition, we developed a modified microwave digestion procedure which provides significantly improved spike recoveries for the waste forms studied.

EXPERIMENTAL SECTION

A Jarrell-Ash Atomcomp 1100 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) upgraded to be equivalent to a Model 61E was used for the analysis of the nonradioactive materials. Glovebox-interfaced instruments, an ARL 3580 ICP-AES and VG PQ II Inductively Coupled Plasma Mass Spectrometer (ICP-MS), were used to obtain data for the radioactive materials. A CEM MDS 2000 temperature- and pressure- controlled microwave oven was used for digestion of the nonradioactive materials. A Floyd remote pressure controlled microwave oven installed in a glove box was used for

digestion of the radioactive materials. Calibration standards were obtained from either NIST or SPEX Industries, Inc. Unless otherwise noted, spikes were added before the digestion step.

TCLP

Effect of Sample Size

Initial TCLP experiments investigated the use of reduced sample sizes while maintaining the 1:20 sample weight:extraction volume ratio required by SW-846 Method 1311 (1). To study this method we used a 2L extractor (100g sample) and a 200mL extractor (10g sample). Process sludge from TA-50 (the radioactive waste processing facility for Los Alamos National Laboratory) was used; this sludge has an activity of about 600dpm/g. The primary radioactive constituent is Am but traces of Pu are present.

Both 100g and 10g samples of TA-50 process sludge were analyzed in duplicate by the SW-846 Method 1311. The resulting leachates were analyzed by ICP-AES. These results are shown in Table 1. The spike recoveries for the samples are given in Table 2. Although recoveries were not satisfactory for Hg these recoveries are consistent for both the 100g and 10g samples.

The results in Tables 1-2 show that this sludge is homogeneous on the 10g scale and that spike recoveries are independent of sample size. The use of smaller samples is desirable because the waste may contain both radioactive and hazardous constituents. When a significantly higher sample activity is encountered both as low as reasonable achievable exposures (ALARA) and contamination control procedures dictate the use of the smallest possible sample. Waste minimization considerations also favor the use of smaller samples.

Table 1. Comparison of TCLP results for 100g and 10g samples.

Element	100g Sludge Sample (mg/mL)	10g Sludge Sample (mg/mL)
Ag	0.05	0.06
As	0.3	0.3
Ba	2.4	2.1
Be	< 0.0009	< 0.0009
Cd	0.02	0.01
Cr	0.08	0.07
Hg	0.6	0.2
Ni	0.7	0.7
Pb	< 0.04	0.04
Se	< 0.06	< 0.06
Tl	< 0.1	<0.1

Table 2. Comparison of spike recoveries for 100g and 10g samples.

Element	100g Sample (mg/mL)	10g Sample (mg/mL)	Spike Level (mg/mL)
Ag	4.0	4.0	5.0
As	5.0	5.1	5.0
Ba	99	96	100
Be	1.1	1.0	1.0
Cd	0.90	0.90	1.0
Cr	4.9	4.9	5.0
Hg	0.10	0.30	0.20
Ni	5.3	5.1	5.0
Pb	4.5	4.4	5.0
Se	1.0	1.1	1.0
Tl	0.80	0.80	1.0

Effect of Matrix on Spike Recovery

Spikes were added to the sludge both before and after TCLP extraction to determine whether there is a matrix adsorption effect for these materials. The results of the ICP-AES analysis of the leachates is shown in Table 3.

Table 3. The effect of sample matrix on spike recovery.

Element	Spiked Before Extraction (% Recovered)	Spiked After Extraction (% Recovered)
Ag	7	81
As	5	100
Ba	67	95
Be	20	100
Cd	47	87
Cr	6	94
Hg	120	200
Ni	92	92
Pb	1	90
Se	3	100
Tl	13	87

The recovery of most of the metals decreases when the spike is added directly to the sludge before extraction. This effect demonstrates the absorption capacity of the sludge matrix. This result has no direct ramifications for meeting the requirements of SW-846 Methods 1311 and 6010A (1,4) but demonstrates that Method 1311 does not recover all of the RCRA analytes from this type of matrix. The recovery of spike

added immediately before instrumental analysis assures the operator of proper instrumental operating parameters (Method 6010A) (4).

MICROWAVE DISSOLUTION AND LEACHING PROCEDURES

Total Dissolution Methods

Total dissolution methods have been investigated and compared to the TCLP. The total dissolution methods will result in less waste production and provide more complete information about the concentration of RCRA elements in the waste.

Investigations of microwave dissolution of synthetic sludges have been performed at the Idaho National Engineering Laboratory (INEL) (2) using a 2:1 mixture of HF and HNO_3. It was found that 2g of synthetic sludge was completely dissolved in 10mL of the acid mixture after microwave treatment (30min, P_{max}=25psi), dilution to 70mL with water, and addition of 1g of boric acid (2). For TA-50 sludge, application of this procedure did not result in total dissolution. This result is not surprising considering the complexity of this matrix and the differences between the synthetic and actual sludges.

Method 3051 Leach

For these studies we used the Floyd microwave oven described in the experimental section. SW-846 Method 3051 (3) was followed as closely as possible within the constraints of the glove box conditions. The primary difference was in the heating cycle. Method 3051 dictates the following conditions: maximum sample size of 0.5g, 10mL of concentrated HNO_3, and "a sequence of power that brings the samples to 175°C in 5.5min and permits a slow rise to 175-180°C during the remaining 4.5min" (3). For all of the experiments described below, the solutions of 0.5g of sample and 10mL of acid were microwaved for 30min with a maximum pressure setting of 25psi. In spite of this difference, we will refer to this method as Method 3051.

Determination of Sample Homogeneity. Because very small amounts of samples are used in the Method 3051 procedure, sample homogeneity becomes very important. For the TCLP Method 1311, the much larger sample size (10-100g) reduces concern about this issue. To study homogeneity we analyzed three different sludges: processor sludge (TRUCON 211) and two batches of sludge that are ultimately cemented to form TRUCON 226. The last two sludges have a higher liquid content and higher radioactivity than the first sludge. For the high-liquid-content sludges (drums 6 and 14) the Method 3051 procedure was further modified: 5mL of the suspension generated by vigorous shaking of the sludge was used instead of 0.5g. All of these sludges appeared inhomogeneous on visual inspection. By reviewing the results of these tests, we also hoped to determine baseline information about the RCRA constituents of these actual sludges.

The results of the homogeneity investigation are given in Tables 4-6. These data illustrate that these samples were homogeneous on the 0.5g (or 5mL) scale. The data also imply that the method of shaking and pipetting the high-liquid-content sludge may be an acceptable sampling method.

Table 4. Results of ICP-AES and ICP-MS analysis of Method 3051 leachates for quadruplicate analysis of TA-50 process sludge.

Element	0.5052g Sample (mg/g)	0.5181g Sample (mg/g)	0.5127g Sample (mg/g)	0.5117g Sample (mg/g)	Average (mg/g)	Standard Deviation
Ag	< 1	< 1	< 1	< 1	< 1	
Ba	680	710	670	660	680	20
Cd	1.9	1.8	1.8	1.8	1.8	0.06
Cr	99	93	86	86	91	6
Hg	15	15	15	15	15	0.2
Pb	370	380	350	340	360	20
Be	< 0.02	< 0.02	< 0.02	< 0.02		
Ni	250	250	230	230	240	9
Sb	< 1	< 1	< 1	< 1		
Tl	< 1	< 1	< 1	< 1		

Table 5. Results of ICP-AES and -MS analysis of Method 3051 leachates for duplicate of TA-50 sludge (drum 14).

Element	Sample A (mg/g)	Sample B (mg/g)	Average (mg/g)	Standard Deviation
Ag	< 1	< 1		
Ba	< 0.5	< 0.5		
Cd	< 1	< 1		
Cr	25	24	24	0.9
Hg	< 0.1	< 0.1		
Ni	17	17	17	0.5
Pb	22	21	22	0.5
Sb	< 1	< 1		
Tl	< 1	< 1		

Comparison of Methods 3051 and 1311. Applying Method 3051 rather than Method 1311 to the analysis of mixed waste samples would enhance waste minimization. Therefore, the performance of these two methods was compared. Data were collected for the TA-50 process sludge described earlier using Methods 1311 and 3051 and ICP-AES analysis. The results are presented in Table 7. As expected, the Method 3051 leach procedure results in higher levels of the RCRA elements in the leachate. However, for all of the elements except Pb, the levels are still below the RCRA limits.

Table 6. Results of ICP-MS analysis of Method 3051 leachates for triplicate analysis of TA-50 sludge (drum 6).

Element	Sample A (mg/g)	Sample B (mg/g)	Sample C (mg/g)	Average (mg/g)	Standard Deviation
Ag	3.0	3.1	3.0	3.1	0.07
Ba	3.9	4.0	3.8	3.9	0.1
Cd	0.46	0.51	0.44	0.47	0.03
Cr	190	210	210	200	10
Hg	0.48	0.51	0.47	0.49	0.02
Ni	48	53	52	51	3
Pb	87	91	88	89	2
Sb	< 1	< 1	< 1		
Tl	< 1	< 1	< 1		

Table 7. Comparison of 3015 microwave digestion to 1311 TCLP extraction.

Method 3051 mg/g	Element	Method 1311 mg/g
<1	Ag	1.1
<17	As	6.0
680	Ba	45
<0.02	Be	<0.02
<0.2	Cd	0.30
91	Cr	<1.5
240	Ni	14
360	Pb	0.40
<4	Se	<1.2
<5	Tl	<2

These results suggest that Method 3051 could be used as a screening procedure. Although higher concentrations of the RCRA elements may be found in Method 3051 leachates, for many cases the levels will still be below RCRA limits. For the samples that produce concentrations above the RCRA limit, Method 1311 can subsequently be performed to determine whether the material exceeds the limits for an acetic acid leach. This type of analytical plan would help decrease the amount of waste produced by sample analysis (<25mL for Method 3051 vs 200mL for Method 1311) and would also decrease potential personnel exposure because of the smaller sample size required for Method 3051 (0.5g for Method 3051 vs 10g for Method 1311).

SURROGATE WASTE ANALYSIS

EPA Methods 3051 and 6010A (3,4) were applied to four model and surrogate waste forms to optimize sample preparation, instrumental parameters, detection limits, and spike recoveries for the RCRA listed elements Ag, As, Ba, Be, Cd, Cr, Ni, Pb, and Se. The surrogate materials include pyrochemical salt precursors NaCl, KCl, and $CaCl_2$, a pyrochemical salt prepared with CeO_2 as a PuO_2 surrogate; and HPQ and Lewatite organic resins. This work is directly applicable to the analysis of TRUCON waste forms including pyrochemical salts (TRUCON 224), solidified inorganic process solids (TRUCON 214), and cemented organic process solids (TRUCON 226).

Because these methods should be equivalent to EPA SW-846 methods (1,3,4), the initial investigations focused on unmodified Method 3051, a microwave HNO_3 acid leach, for the sample preparation step. The samples were analyzed by ICP-AES. The digestion procedure was modified as required to produce acceptable spike recoveries for each of these surrogate wastes.

Method 3051 Digestion

A CEM MDS 2000 temperature- and pressure-controlled microwave oven and PFA Teflon digestion vessels were used for these experiments. The samples were heated with 10mL of concentrated HNO_3 in the microwave, which was programmed so that a maximum pressure of 90psi was maintained in the digestion vessels for 4.5min (as required by Method 3051, T=155-165°C). The time required to reach the maximum pressure ranged from 5 to 8min. Samples were then diluted to 100mL with millipore water. Our preliminary investigations focused on determining the optimum sample size and spike recoveries for this method.

Effect of Salt Concentration on Spike Recovery. For these experiments we used the pyrochemical salt precursors at concentrations ranging from 0.15g/100mL to 1.0g/100mL. The results of ICP-AES analysis are given in Tables 8-10. Analyte recoveries were increasingly suppressed with increasing salt concentration. The optimum concentration was 0.15g/100mL.

Although it is not reflected in Tables 8-10, another problem results from use of high salt concentrations. Under such conditions the tip of the ICP torch becomes encrusted with salt and ultimately extinguishes within 2 to 3h. This salt build up would be unacceptable for routine analysis of these material types. Based on this observation and the recovery results, the 0.15g/100mL concentration was used for the remaining studies of the precursor salts.

Table 8. Spike recoveries (%) from Method 3051 digestion of $CaCl_2$ as a function of concentration.

Element	1.0g/mL	0.5g/mL	0.25g/mL	0.15g/mL
Ag	16	8	36	32
As	72	84	76	82
Ba	78	88	84	84
Be	74	92	84	94
Cd	76	94	76	82
Cr	68	76	74	80
Ni	58	70	74	80
Pb	68	84	56	60
Se	82	94	84	92

Table 9. Spike recoveries (%) from Method 3051 digestion of NaCl as a function of concentration.

Element	0.5g/mL	0.25g/mL	0.15g/mL
Ag	9.4	18	22
As	84	84	86
Ba	110	110	110
Be	84	84	86
Cd	96	84	86
Cr	88	94	92
Ni	82	90	88
Pb	92	66	92
Se	98	96	96

The Ag recoveries were unacceptable at all concentrations. Pb recoveries were also low, generally at or below the ±25% limits set forth in Method 6010A (4).

Table 10. Spike recoveries (%) from Method 3051 digestion of KCl as a function of concentration.

Element	0.5g/mL	0.25g/mL	0.15g/mL
Ag	8.0	18	17
As	88	86	86
Ba	110	110	120
Be	88	86	84
Cd	98	86	84
Cr	90	94	94
Ni	84	94	92
Pb	94	72	70
Se	100	98	98

Modified Method 3051

Because of the poor Ag and Pb spike recoveries produced by the Method 3051 leach, we developed and tested a Modified Method 3051 microwave leach. For this procedure 7.5mL of concentrated HCl and 2.5mL of concentrated HNO_3 were added to the sample. The maximum pressure and hold time were the same as described above for Method 3051 (90psi, 4.5min). Investigations were limited to the lower salt concentrations (0.15-0.25g/100ml) at which suppression of spike recoveries decreased.

Analysis of Pyrochemical Salt Precursors. Using the modified method for the pyrochemical salt precursors produced greatly enhanced Ag and Pb spike recoveries for all three precursor salts as shown in Tables 11-13. Another result of addition of HCl to the acid matrix was the ability to use higher salt concentrations without the suppression effects observed in a HNO_3 only matrix (Tables 8-10). The ICP torch was also less prone to the residue problems discussed above and, therefore, was more stable and less likely to extinguish during the analytical procedure.

Table 11. Spike recoveries (%) for $CaCl_2$ using the Modified Method 3051 leach.

Element	0.5g/mL	0.25g/mL	0.15g/mL
Ag	110	110	100
As	100	100	89
Ba	110	110	100
Be	110	110	96
Cd	100	100	84
Cr	100	100	92
Ni	94	96	88
Pb	100	100	94
Se	100	110	90

Table 12. Spike recoveries (%) for NaCl using the Modified Method 3051 Leach.

Element	0.5g/mL	0.25g/mL	0.15g/mL
Ag	100	100	98
As	100	100	95
Ba	100	100	98
Be	100	100	100
Cd	100	98	110
Cr	100	100	100
Ni	98	96	100
Pb	100	98	100
Se	100	98	98

Table 13. Spike recoveries (%) for KCl using the Modified Method 3051 Leach.

Element	0.5g/mL	0.25g/mL	0.15g/mL
Ag	100	98	92
As	96	92	89
Ba	110	110	98
Be	96	92	92
Cd	96	92	100
Cr	100	98	94
Ni	100	98	92
Pb	100	98	94
Se	110	98	91

Analysis of a Pyrochemical Salt Surrogate. A Direct Oxide Reduction (DOR) process surrogate pyrochemical salt was prepared by heating $CaCl_2$, Ca metal, and CeO_2 in a MgO crucible at 850°C (5). The product from this reaction was a heterogeneous solid. The solid was sampled by breaking the large chunk of product with a hammer and then selecting a piece of the material which contained all of the visually observable components. These components include $CaCl_2$, CeO_2, $CeOCl_2$, and Ce metal. This piece was subsampled in an analogous fashion.

Because of the superior spike recoveries obtained with Modified Method 3051 for the pyrochemical salt precursors, this method was used exclusively for the digestion of the surrogate samples. Concentrations in the 0.15g/100mL range were used because of the advantages determined during the investigations of the precursors. The results given in Table 14 indicate problems with As and Se recoveries for this matrix. No concentration dependence was observed for the As and Se recoveries; for some cases the more concentrated solutions showed better spike recovery performance. This result suggests that sample inhomogeneities were responsible for the variable recoveries.

Table 14. Spike recoveries (%) for Modified Method 3051 digestion of the pyrochemical salt surrogate.

Element	0.223g /100mL	0.154g /100mL	0.126g /100mL	0.116g /100mL	0.114g /100mL	0.103g /100mL
Ag	100	100	92	100	100	98
As	58	72	17	25	49	50
Ba	110	110	100	100	96	96
Be	100	98	100	94	100	100
Cd	110	120	110	110	120	120
Cr	100	98	88	84	96	96
Ni	92	92	100	96	110	110
Pb	90	94	90	90	98	96
Se	75	79	68	69	93	89

Wavelength scans were performed over the As and Se spectral regions for a spiked acid blank, a surrogate blank, a spiked surrogate, and a 1000ppm Ce solution. Potential interferences from Ce are clearly present as shown in Figure 1. This result explains the variability in recoveries for the samples: because of the inhomogeneity of the surrogate salt, the amount of Ce present will not necessarily correlate with sample size. Because the actual waste will contain Pu and not Ce, determination of a reliable interference correction method was not pursued.

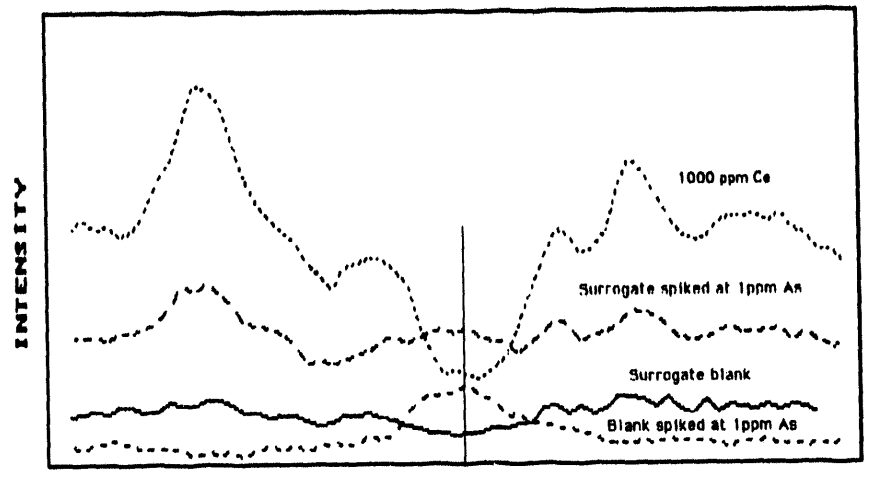

Figure 1. As and Se spectral regions showing interferences from Ce in the surrogate pyrochemical salt matrix. The peaks in the surrogate blank spectrum are from Ce.

The Modified Method 3051 digestion was also applied to pieces of the MgO crucible. At concentrations above 0.1g/100mL, problems were noted with recoveries for Ag and As. However, as the MgO loading was decreased, satisfactory recoveries were obtained, as shown in Table 15.

Table 15. Spike recoveries (%) obtained for the MgO crucible using the Modified Method 3051 digestion.

Element	0.216g/100mL	0.165g/100mL	0.112g/100mL	0.106g/100mL
Ag	64	62	86	100
As	74	80	96	95
Ba	110	100	100	100
Be	90	92	110	110
Cd	100	100	110	110
Cr	94	92	98	100
Ni	96	94	100	100
Pb	96	96	100	100
Se	87	89	100	100

Analysis of Ion Exchange Resins. When the Modified Method 3051 was applied to digestion of both the HPQ and Lewatite organic ion exchange resins, the formation of gaseous decomposition products resulted in low temperatures (83±2°C) at the maximum pressure (90psi). The Ag recoveries dropped to near the 25% limit, and the Cd recoveries were unacceptable for the Lewatite resins at concentrations of about 0.5g/100mL. The HPQ resins showed the same trends, even at concentrations of 0.25g/100mL. Scans over the Cd region (Fig. 2) showed no spectral interferences or background problems that could be associated with the low recoveries. The peak shapes for a 1ppm Cd sample and the 0.5ppm (50%) Cd recovery from a resin sample are very similar; the large intensity disparity suggests Cd holdup in the porous resin beads. Therefore, the HCl/HNO_3 digestion method was further modified.

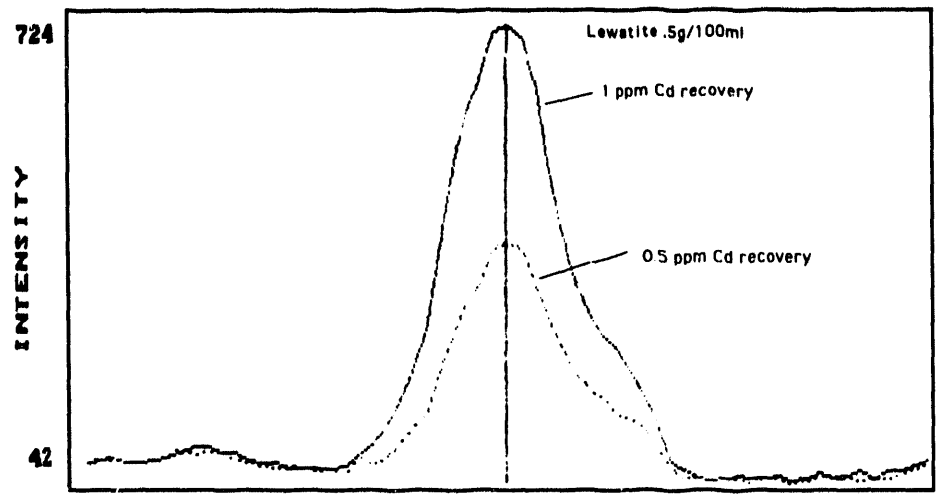

Figure 2. Scans over the Cd for Lewatite (0.5/100ml) spiked at 1ppm Cd.

The first attempt at modification was to implement a four-stage heating process based on the CEM procedure for anion resin (6). During each stage of the heating process, the maximum pressure setting was gradually raised. The pressure settings used for the four-stage digestion were 40, 80, 120 and 175psi. The

time-at-pressure setting was 5min for each of the first three stages and 10min for the fourth stage. The HPQ resin spike recoveries for Cd using this method averaged 76%. However, the rupture disks (rated at 200 psig) failed for two of the six digestion vessels that were tested. A two-stage heating process was then evaluated. The microwave oven was programmed to heat the vessels to a maximum pressure of 90psi for 30min. The temperature during this cycle was 97°C for both resins tested. The vessels were cooled to room temperature, vented, and then heated for an additional 30min at 90psi. During the second cycle the temperature in the vessels ranged from 115 to 119°C. The results in Tables 16-17 clearly show the enhanced Cd recoveries for the two stage heating profile relative to the single-step digestion.

Table 16. Spike recoveries (%) for Lewatite resin Modified Method 3051 digestions.

	4.5min Heating Profile			Two-Stage 30min Heating/Venting Profile		
Element	Spike Blank	0.5284g/ 100mL	0.5317g/ 100mL	Spike Blank	0.1185g/ 100mL	0.1426g/ 100mL
Ag	100	76	78	110	100	98
As	97	99	100	110	100	100
Ba	96	100	100	110	110	110
Be	100	100	100	110	110	110
Cd	110	47	54	120	85	85
Cr	98	100	98	110	110	110
Ni	100	100	100	110	110	120
Pb	100	88	88	110	96	100
Se	99	100	100	110	110	120

Table 17. Spike recoveries (%) for HPQ resin Modified Method 3051 digestions.

	4.5min Heating Profile			Two-Stage 30min Heating/Venting Profile		
Element	Spike Blank	0.2524g /100mL	0.2560g /100mL	Spike Blank	0.1123g /100mL	0.0955g /100mL
Ag	110	94	58	84	96	98
As	110	110	110	110	110	110
Ba	100	100	100	110	100	110
Be	110	110	110	110	110	110
Cd	110	53	53	120	74	74
Cr	110	110	110	110	110	110
Ni	110	110	110	110	110	110
Pb	110	94	100	110	100	100
Se	110	110	110	110	110	110

Although both the four-stage and the two-stage digestion cycles produced acceptable spike recoveries, all subsequent studies will employ the two-step method. The lower maximum pressures obtained (90psi vs 175psi) did not result in any rupture disk failures.

Summary of Surrogate Studies. Method 3051 does not produce acceptable spike recoveries for the surrogate wastes studied. The Modified Method 3051 digestion we have developed using aqua regia leads to ±25% spike recoveries from the MgO crucible and the pyrochemical salt precursors NaCl, KCl, and $CaCl_2$. For the pyrochemical salt surrogate, Modified Method 3051 produced ±25% spike recoveries for all elements studied except As and Se. The low recoveries for these elements were attributed to Ce interferences. Because Ce will not be an interferent in the actual pyrochemical salt waste, corrections for this interferent were not identified. Use of a two-step microwave heating program for our Modified Method 3051 resulted in acceptable spike recoveries for all elements in the Lewatite resin. For the HPQ resins the two-step procedure led to acceptable recoveries for all elements except Cd which was recovered at 74%.

This information can be directly transferred to the analysis of actual TRUCON waste forms and clearly demonstrates that EPA SW-846 Method 3051 (3) will not be applicable to the digestion of these materials. The HCl/HNO_3 leach method that we have developed shows the potential for application to a wide range of waste materials. As demonstrated, specific digestion conditions may have to be developed for some waste forms, especially those containing organic components. However, the availability of a baseline method, the HCl/HNO_3 leach, and the knowledge of which applications may require additional development will facilitate the fine-tuning of the HCl/HNO_3 digestion method.

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RAPID ANALYSIS OF MIXED WASTE SAMPLES VIA THE OPTICAL EMISSION FROM LASER INITIATED MICROPLASMAS

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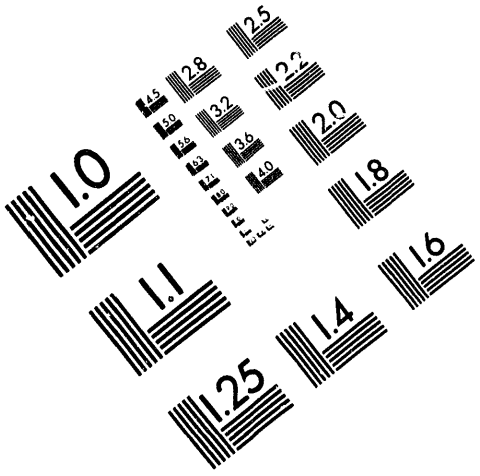
ABSTRACT. Wavelength resolved optical emission from laser initiated microplasmas in samples containing Pu, Am, Pb, Cr, and Be was used to determine elemental compositions. Traditionally, samples of this type are analyzed by neutron activation, X-ray fluorescence, atomic absorption, inductively coupled plasma - atomic emission spectroscopy, and inductively coupled plasma mass spectroscopy. Analysis via the traditional analytical spectroscopic techniques involves extensive sample separation and preparation which results in the generation of significant quantities of additional waste. In the laser based method, little to no sample preparation is required. The method is essentially waste free since only a few micrograms of material is removed from the sample in the generation of the microplasma. Detection limits of the laser based method typically range between sub ppm to tens of ppm. In this report, the optical emission from samples containing Pu, Am, Pb, Cr, and Be will be discussed. We will also discuss the essential elements of the analysis method.

INTRODUCTION

Traditionally, the elemental analysis of mixed waste containing radioactive and other environmental sensitive elements (for example Pb, Cr, and Be) is obtained using inductively coupled plasma - atomic emission spectroscopy (ICP-AES)(1,2), neutron activation, x-ray fluorescence, atomic absorption (AA)(3), and inductively coupled plasma - mass spectroscopy (ICP-MS)(4). Such methods can involve extensive sample separation and preparation. A considerable amount of the analysis time is devoted to selecting the proper dissolution matrix or sample form. Thus in many cases, significant quantities of additional waste is generated. The analysis of mixed waste using the techniques listed above typically take a minimum of hours and in many cases days or weeks.

In the laser based method, short pulses from a laser are focused onto the surface of a sample where a microplasma is generated . The optical emission from the microplasma is then collected and analyzed to determine elemental composition. This method is commonly referred to as laser induced breakdown spectroscopy (LIBS) here at Los Alamos. Again, little to no sample separation or preparation is required. In the generation of the microplasma, only a few micrograms of material is removed from the sample. Therefore very little to no waste is generated using this method. However, for quantitative measurements calibration standards must be prepared. Once good calibration standards and curves have been obtained, quantitative analysis of samples of interest can be performed with little to no further sample preparation.



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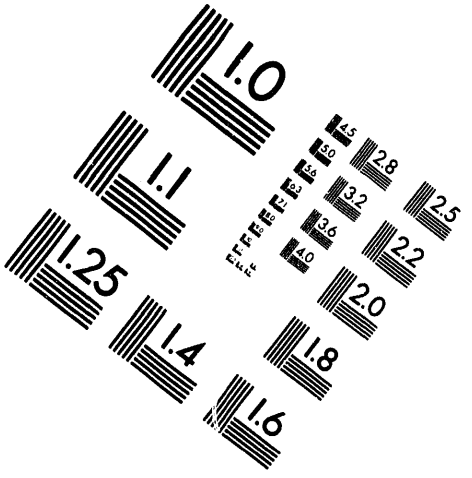

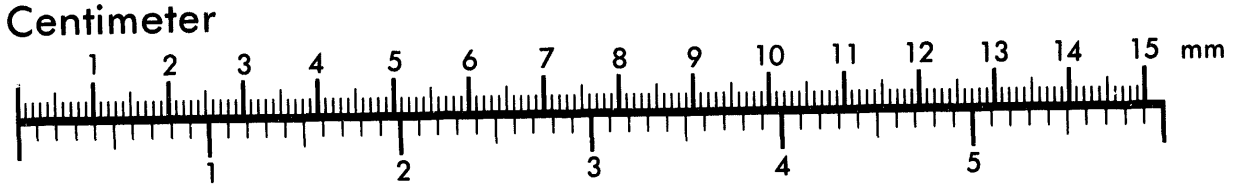

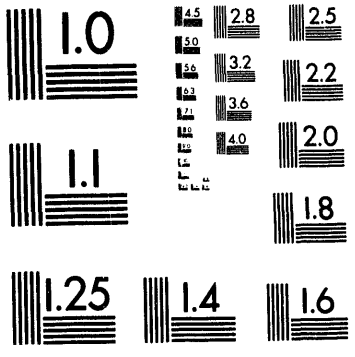

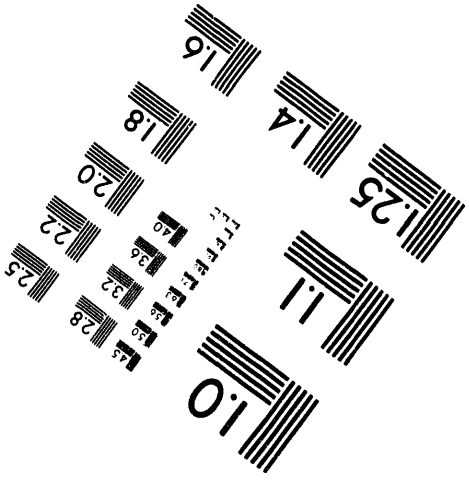

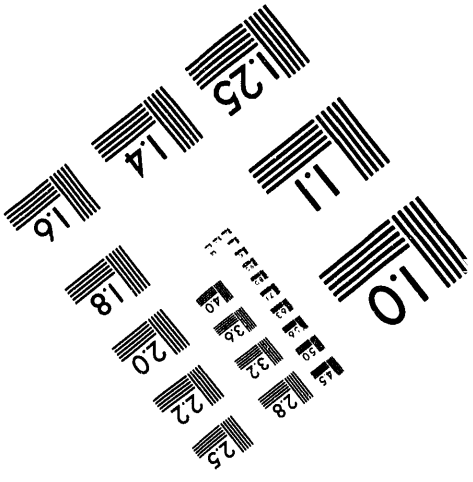

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The analysis times of the laser method are on the order of a few minutes.

Although all of the elements in the sample are excited at the same time, spectral discrimination is accomplished via temporal and wavelength dispersive methods . Again, the microplasma is generated via excitation from short laser pulses (10 ns). By varying the time between when the plasma is created and the optical emission is observed, one can essentially control the population of states for an element or a group of elements. Initially, when the plasma is created the population of states is a maximum and the observed optical emission is a white light continuum(5). This emission result from the decay of the population of high ionic and neutral states from the elements in the sample. As the observation time is delayed relative to the initial time when the plasma was created, the population of states decreases and atomic line type optical emission is observed. For delay times of a few ns to μs, the emission is essentially dominated by emission from ionic states. At longer delay times (tens of μs), neutral emission tends to dominate.

In this report, we will discuss the LIBS technique, results from samples containing Pu, Am, Pb, Cr, and Be., and applications of the technique to remote monitoring of environmental sensitive areas.

EXPERIMENTAL

A schematic of a typical LIBS apparatus is shown in Fig 1. In this diagram, the output from a Nd:Yag laser is focused onto the surface of a sample where a microplasma is generated. The laser operates at 1064 nm and the pulse length is 7 - 10 ns. Depending upon the coupling of the laser light to the sample 10 to several hundred mJ of excitation energy is used to generate the microplasma. The emission from the plasma is then collected and imaged onto the slit of the monochromator. We used a 1/3 or 1/2 m monochromator for the measurements discussed in this report. The wavelength resolved emission from the monochromator is detected with a Tracor Northern or Princeton Instruments 1024 element linear diode array detector. Temporal resolution of the emission from the plasma is accomplished by gating the diode array detectors.

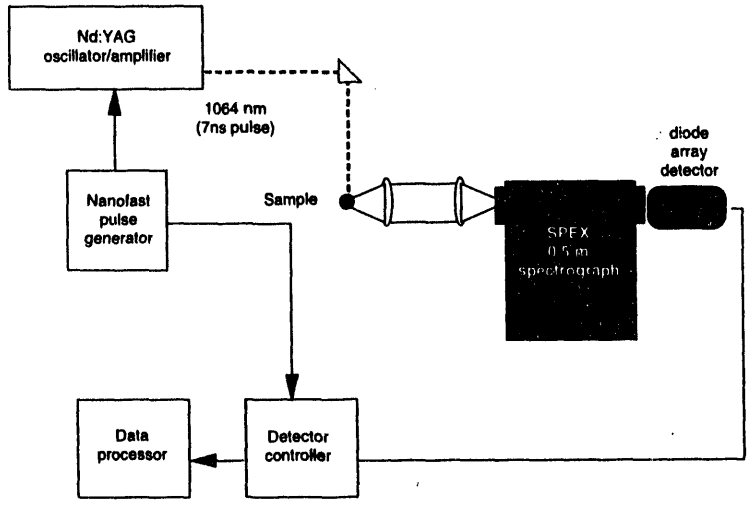

Figure 1. Laser induced breakdown spectroscopy apparatus.

RESULTS AND DISCUSSION

The atomic emission spectra of plutonium and americium contains many lines due to the complicated electronic structure of the respective atoms(6,7). Again, the microplasma created on the surface of the plasma is generated by a short pulse laser (~ 10 ns). The optical emission from the respective elements in

the sample is therefore transient in nature. Initially, many ionic states and high excited states of the elements in the sample are excited. Therefore, if one chooses to observe the plasma with zero delay, only a structureless white light or a background continuum is observed. As the delay time is increased, atomic like line emission is observed. Typically, for delay times of a few microseconds atomic ionic type emission is observed. At longer delay times (tens of μs), atomic neutral type emission is observed(8).

The atomic emission spectra of a sample containing plutonium in a NaCl/KCl salt matrix is shown in Fig 2. The delay time for this spectrum was 0.7 μs . The emission at this point is primarily ionic. By changing the delay to 1.7 μs, the spectrum shown in Fig 3 is observed. The spectrum shown in Fig 3 is considerably less congested and the background continuum emission has been reduced by approximately a factor of 4. In this way one can use the transient nature of the technique to achieve a desired level of spectral discrimination. The spectra shown in Figs 2 and 3 were recorded on a 1/2 m monochromator. Spectral discrimination can also be improved by using a longer path length monochromator. We have installed a 1.26 m monochromator in our LIBS apparatus and is in the process of testing it. The atomic emission spectrum of a sample containing americium oxide is shown in Fig 4. Again, the delay time was 0.7 μs and the data was recorded on a 1/2 m monochromator.

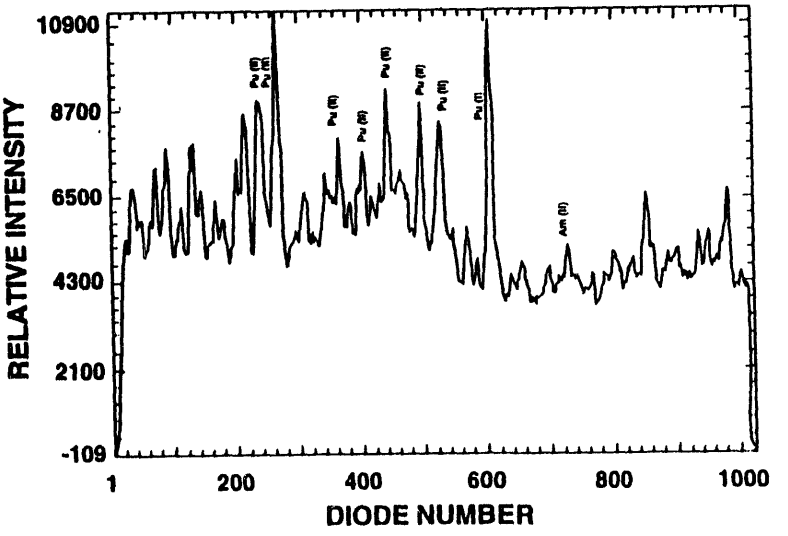

Figure 2.Laser induced emmission spectrum of plutonium in NaCl/KCl in the 450 nm region.

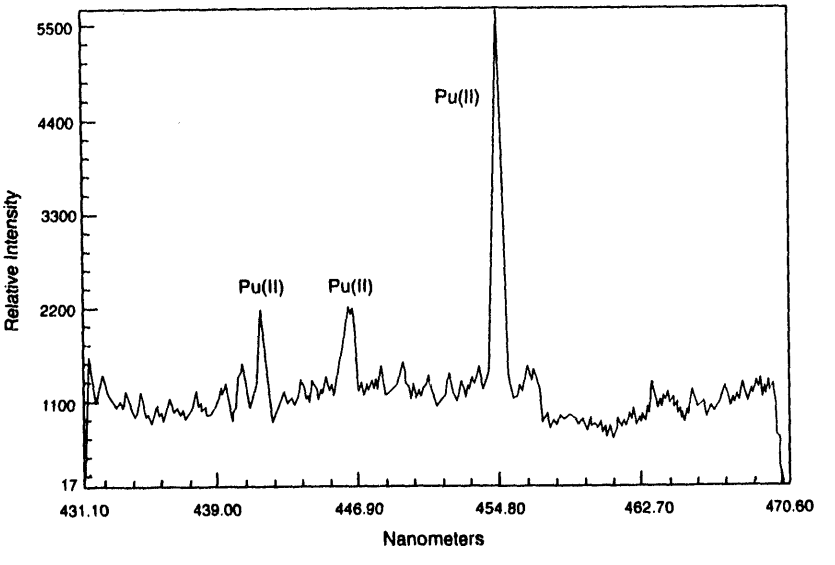

Figure 3.Atomic emission spectrum of plutonium NaCl/KCl with a delay of 1.7 μs.

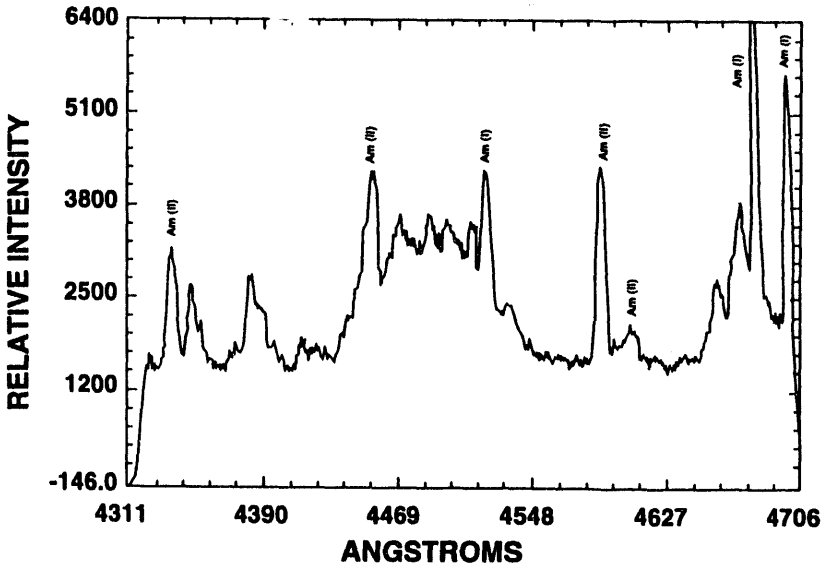

Figure 4. Atomic emission spectrum of sample containing americium in the 450 nm region.

Preliminary assignments for several ionic emission lines for plutonium and americium have been made and are shown in Table 1. The data from Fred et. al(7). and J. R. Reader et. al(9) (National Standard Reference Data) were used to make the assignments. We have not determined the detection limits for plutonium and americium but the detection limit for uranium in solution has been measured by Wachter and Cremers here at Los Alamos(10). The detection limit for uranium in 4 molar nitric acid was 0.1 g/L. We expect that the detection limits for plutonium and americium in solution to be similar. The detection limits for plutonium and americium in solids (soils, alkali salts, and other solid waste forms) and liquids (acid solutions, water, other radioactive waste streams at Los Alamos) will be determined.

Table 1.Atomic emission spectral lines of plutonium and americium.

Observed Wavelength (angstroms)	Assignment
4324.57	Am(II)
4379.91	Pu(II)
4385.35	Pu(II)
4404.90	Pu(II)
4461.36	Am(II)
4461.65	Pu(II)
4472.79	Pu(II)
4493.78	Pu(II)
4504.91	Pu(II)
4509.45	Am(I)
4536.15	Pu(II)
4575.56	Am(II)
4662.79	Am(I)
4681.65	Am(I)
4712.90	Am(I)

Atomic emission spectra for Cr in soil and a sample containing Be are shown in Figs 5 and 6 respectively. Recently, Han and Cremers have completed a study using the LIBS technique to measure the concentration of Cr, Pb, and Be in soil samples(11). Detection limits of 2 ppm for Cr and Pb and 0.1 ppm for Be was determined.

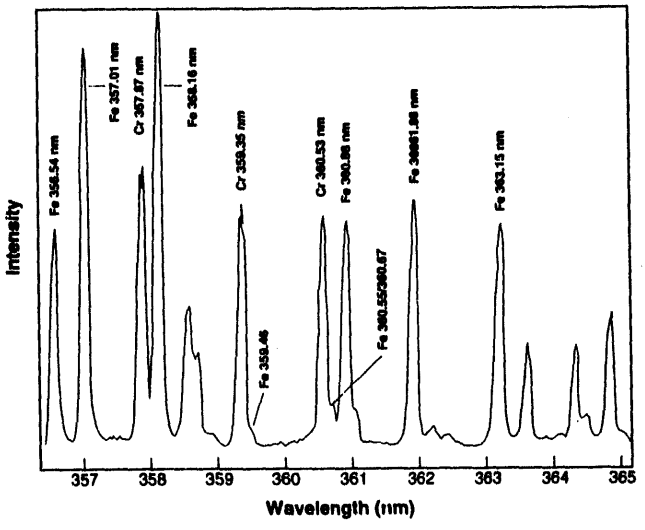

Figure 5.Atomic emission spectrum of a soil sample containing chlorium.

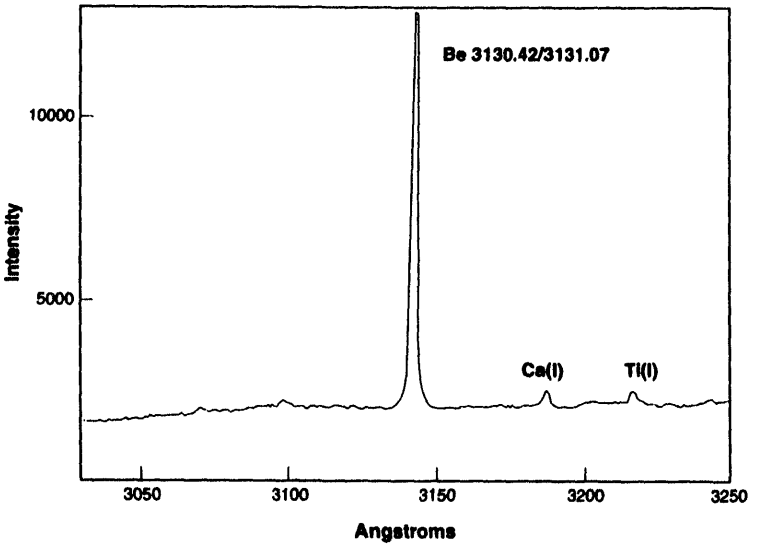

Figure 6. Atomic emission spectrum of a soil sample containing baryllium.

Recently, we have combined the LIBS technique with fiber optic technology to enhance remote monitoring of the elemental composition of samples in harsh environments such as waste tanks, gloveboxes for handling radioactive samples, and soil samples above and below ground. Fiber optic technology has progressed to the point now where high power (MW) short pulse laser beams (pulse lengths of ps and ns) can be transported through fiber optic cables with little loss of power. Transmission efficiencies greater than 99.99 % per meter have been achieved. We have been investigating the use of a 1.5 mm fiber optic cable for remote elemental analysis of samples in harsh environments. A schematic of a fiber optic coupled LIBS system that we have been testing is shown in Fig 7. The essential components of this system are the same as those shown in Fig 1. The difference is the method by which the laser beam is transported to the sample and the emission from the sample is collected and imaged onto the slit of the monochromator. In this apparatus, the excitation laser is coupled into the fiber optic cable by a telescope . The excitation energy is then coupled onto the sample by an output telescope. The emission from the plasma is then re-imaged back down the optical fiber to a beam splitter where it is reflected and collected by a lens and a fiber optic bundle. The output from the fiber optic bundle is imaged onto the slit of the monochromator. We have tested fiber optic cables up to 5 m in length. However, in principle fiber optic cables of many meters can be used. Collection of the emission from laser generated plasmas has been reported in the past(12).

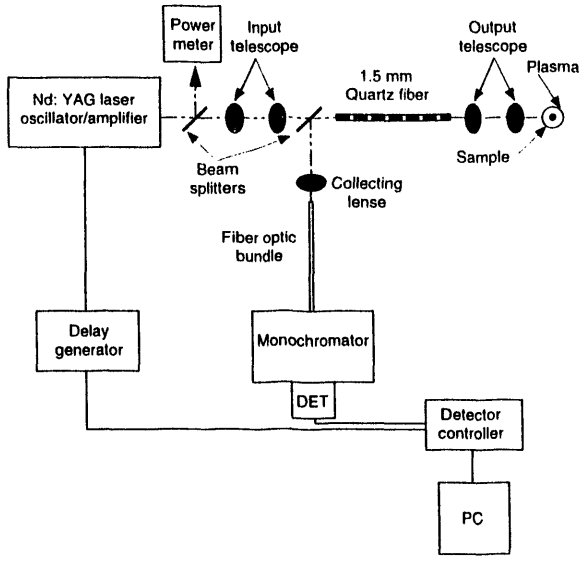

Figure 7. Schematic of a LIBS apparatus combined with fiber optic cable.

CONCLUSIONS

The LIBS technique can be used to measure the elemental composition of samples from a wide range of matrix forms. The waste forms investigated include mixed waste, contaminated soils, alkali salts, and acid solutions. However, samples of solids, liquids , and gases can be analyzed using this technique. Typical detection limits range between a few to hundreds of ppm and depend upon the sample and experimental conditions. Compared to traditional analytical analysis techniques mentioned above, this technique can be operated in real to near real time. That is , the analysis can be performed in a few minutes. Since only a few micrograms of material is removed per laser pulse, analysis via the LIBS technique generates little to no waste. Instruments based upon this technique can be made small and portable which allow field characterization and environmental site remediation efforts to be monitored in real time. Finally, coupling the LIBS technique with fiber optic cables allow the full potential of remote monitoring of samples to be exploited. Thus remote monitoring of mixed waste samples and samples in harsh environments can be obtained.

ACKNOWLEDGMENTS - We want to think personnel in NMT-3 here at Los Alamos for providing the radioactive samples. This work was performed under the auspices of the U. S. Department of Energy.

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CHAPTER 14

Treatment of Mercury Contaminated Wastes and Bioprocessing

PROCESSING RESULTS OF 1,800 GALLONS OF MERCURY AND RADIOACTIVELY CONTAMINATED MIXED WASTE RINSE SOLUTION

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ABSTRACT. Mercury-contaminated rinse solution was successfully treated at the Idaho National Engineering Laboratory. This waste was generated during the decontamination of the Heat Transfer Reactor Experiment 3 reactor shield tank. Approximately 6.8 m^3 (1,800 gal) of waste was generated and placed into 33 drums. Each drum contained precipitated sludge material ranging from 2–25 cm in depth, with the average depth of about 6 cm. The pH of each drum varied from 3–11. The bulk liquid waste had a mercury level of 7.0 mg/L, which exceeded the Resource Conservation and Recovery Act limit of 0.2 mg/L. The average liquid bulk radioactivity was about 2.1 pCi/mL, while the average sludge contamination was about 13,800 pCi/g. Treatment of the waste required separation of the liquid from the sludge, filtration, pH adjustment, and ion exchange. The resulting solution after treatment had mercury levels at 0.0186 mg/L and radioactivity of 0.282 pCi/mL.

INTRODUCTION

Scope

This report addresses the processing of approximately 6.8 m^3 (1,800 gal) of mercury-contaminated mixed waste, henceforth referred to as the Test Area North (TAN) mercury-contaminated rinse solution at the Idaho National Engineering Laboratory (INEL). The objective of this paper is to detail the methods by which the waste was processed and describe final waste forms and ultimate disposal of each waste form. Included in this report are details of processing problems and recommendations for future processing of similar wastes.

Background

The TAN mercury-contaminated rinse solution was produced from the decontamination of the Heat Transfer Reactor Experiment 3 (HTRE-3) reactor shield tank. This reactor was designed as part of the experimental airplane engine program. Shielding for the reactor was provided by a shield tank filled with approximately 1,500 gal of mercury. This reactor has since been put on display at the Experimental Breeder Reactor I (EBR-I) museum.

Prior to the HTRE-3 reactor being sent to EBR-I for display, the residual mercury was removed by rinsing the shield tank with 30 wt% nitric acid solution. After rinsing the shield tank, the pH of the solution was increased to about 10 by adding 50 wt% sodium hydroxide. Sodium sulfide was then added to convert the mercury to an insoluble mercury sulfide. Aluminum sulfate was then to be added to act as a flocculating agent. The solution was then to be neutralized to a pH of 7 and filtered through a 5-μ filter.

Originally, it was anticipated that the resulting waste would pass Resource Conservation and Recovery Act (RCRA) limits and then be disposed of as a nonhazardous, nonradioactive waste. However, the solution did not pass RCRA limits and radioactivity was detected. The mixed waste was placed into 33 polyethylene, 55-gal drums, and the drums of waste were placed into the Mixed Waste Storage Facility (MWSF) at the INEL. Information from the waste characterization report and results from analyses performed on the waste indicate that each waste drum has a different pH and metals concentration.

WASTE TREATMENT

The TAN mercury-contaminated rinse solution was treated as part of a treatability demonstration of liquid mixed wastes at the INEL. Several similar mixed wastes have been identified at the INEL for potential treatment by ion exchange. The processing of the 6.8 m^3 of TAN mercury-contaminated rinse solution waste was to evaluate the treatability of this and similar wastes on a large scale by ion exchange and the requirements of a treatment system for future processing.

Prior to treatment of the 6.8 m^3, treatability studies were performed on samples of the waste at the Test Reactor Area (TRA) radiochemistry lab located at the INEL (1). After completion of the treatability studies, treatment facility and treatment process options were evaluated and a processing scheme was developed. The following sections detail the processing of the TAN mercury-contaminated rinse solution. Three processing trials were required to reduce the mercury levels of the waste to acceptable limits, and are denoted as Trials 1, 2, and 3.

Treatability Studies

Treatability studies were performed on samples of the waste to evaluate treatment options and recommend a treatment plan. The results of the treatability studies are summarized here; detailed results are in Ref 1.

Six of the 33 drums were sampled to perform treatability studies. The samples indicated that the waste had both a liquid phase and a solid sludge phase of 5–8 cm at the bottom of each drum. The liquid was separated from the solids by using a 0.45-μ filter, and both the liquid filtrate and the solids were analyzed for metals and radioactivity.

A metals analysis was performed on the six samples, and mercury and lead were found to be above the RCRA limits of 0.2 mg/L and 5.0 mg/L, respectively. The six samples had a wide range of concentrations for lead and mercury. Most of the mercury values were over the RCRA limit, ranging from 0.133 to 4.68 mg/L with an average of 1.156 mg/L. Only one lead value was over the RCRA limit, ranging from 0.622 to 8.10 mg/L with an average of 3.03 mg/L. The total activity of the filtrate was low, ranging from 2.2 to 74 pCi/mL with an average of 21 pCi/mL. The total activity of the sludge was much higher, ranging from 1,050 to 40,000 pCi/g with an average of 13,800 pCi/g.

All the samples had very high concentrations of sodium, reading beyond the capability of the analytical instrument and indicating that the sodium sulfide was probably added. Also, some of the samples had high concentrations of aluminum while others had almost no aluminum, indicating that some of the containers may have had aluminum sulfate added. The pH of the samples ranged from less than 3 to greater than 10.

Ion exchange experiments were run in a glass column, 1.5 cm in diameter and 20–25 cm tall. The following conclusions and recommendations for large scale processing of the waste were made:

- Results of the treatability study indicate that the waste can be treated to remove the hazardous heavy metals of mercury and lead by use of an ion selective resin. The two recommended selective ion resins were: GT-73 produced by Rhom and Hass, and S-920 produced by Purolite. The first resin, GT-73, proved to be effective with mercury and lead removal, but was not commercially available in bulk. A total of 7 kg was obtained for use. The second resin, S-920, was then evaluated and found to be effective.
- Heavy metal removal was most efficient at acidic conditions, pH 4 – 6, but also was effective under caustic conditions, pH 8 – 10. A pH drop of about two points occurred during processing of the waste.
- Heavy metal removal was effective at a flow rate of 10 – 12 bed volumes per hour.
- All the resins tested passed the RCRA toxicity characterization leaching procedure (TCLP) metals testing after treatment of the waste.
- The sludge failed for TCLP lead, but passed all other TCLP metals. This indicated that the filters would probably become a mixed waste.

Treatment at the PWTU

The 6.8 m^3 of liquid waste was treated at the Portable Water Treatment Unit (PWTU). The PWTU was originally designed to treat well water contaminated with low levels of radioactive isotopes and trichloroethylene at the INEL. The PWTU contains a filtering system, activated carbon beds, resin columns for radioactive isotope removal, and pH adjustment system as shown in Fig. 1.

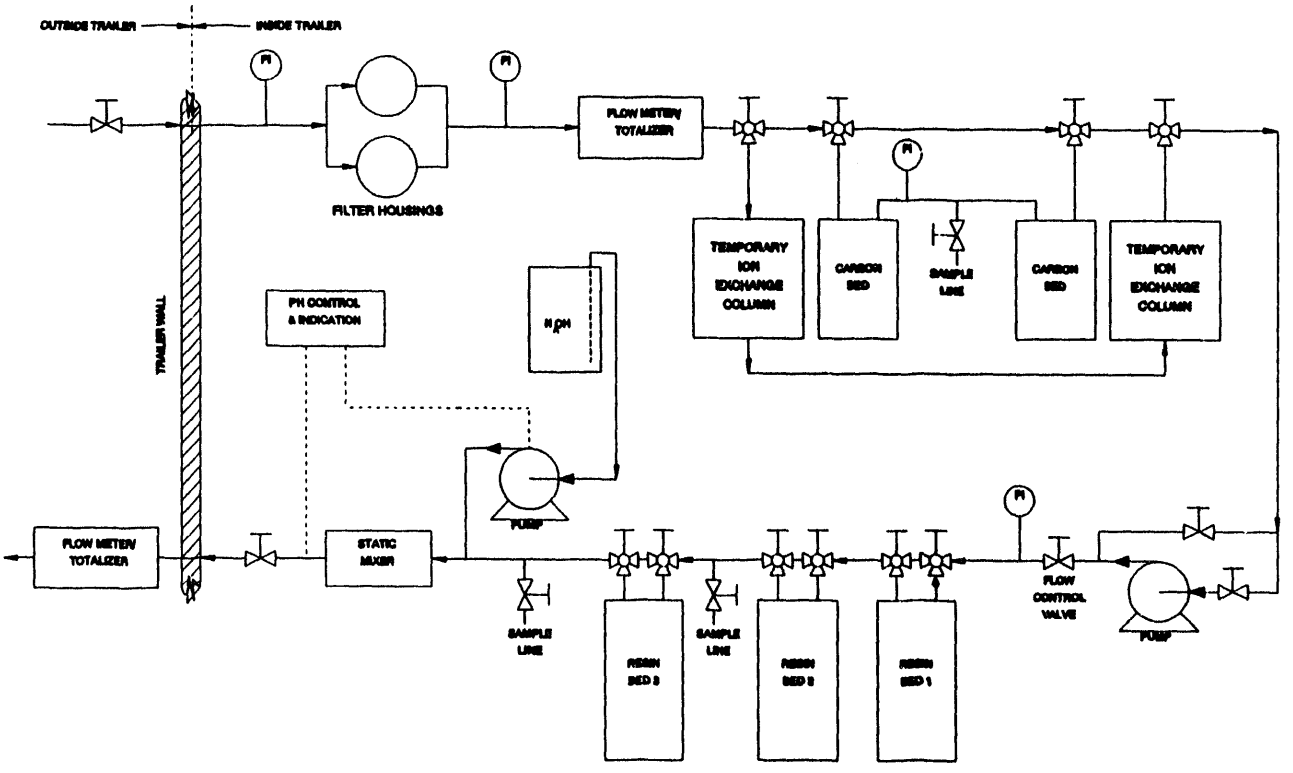

Figure 1. PWTU flow diagram.

All processing of the waste could not take place at the PWTU. The radioactivity of the waste exceeded the limits specified in the PWTU safety analysis report (SAR). However, because most of the radioactivity was in the sludge portion, the liquid portion could be processed at the PWTU if it was separated from the sludge. The liquid was separated from the sludge at the TAN Hot Shop located at the INEL.

In order to process the liquid waste at the PWTU, modifications to the system were required. The existing columns in the PWTU contained C-100H resin from Purolite. This resin is not capable of removing heavy metals to required concentrations below the RCRA limit. To remove the heavy metals from the waste, ion exchange columns packed with GT-73 and S-920 were installed. Also, the PWTU did not have a means to adjust the pH of the waste prior to ion exchange, so the pH was adjusted while the waste was in the waste drums.

Figure 2 shows the flow diagram for the treatment of the waste. The waste was first removed from the MWSF and brought to the TAN Hot Shop, a trip of about 45 mi. The liquid waste was then separated from the sludge. The sludge was combined into four drums and sent back to the MWSF for future treatment. The liquid portion was pumped into clean 55-gal drums and taken to the PWTU storage area. At the PWTU the waste had the pH adjusted to 7–8. The waste was then processed in the PWTU and discharged to two polyethylene storage tanks. Upon verification of the treatment by sampling and analysis, the waste would be discharged to the waste pond at TAN, TSF-07.

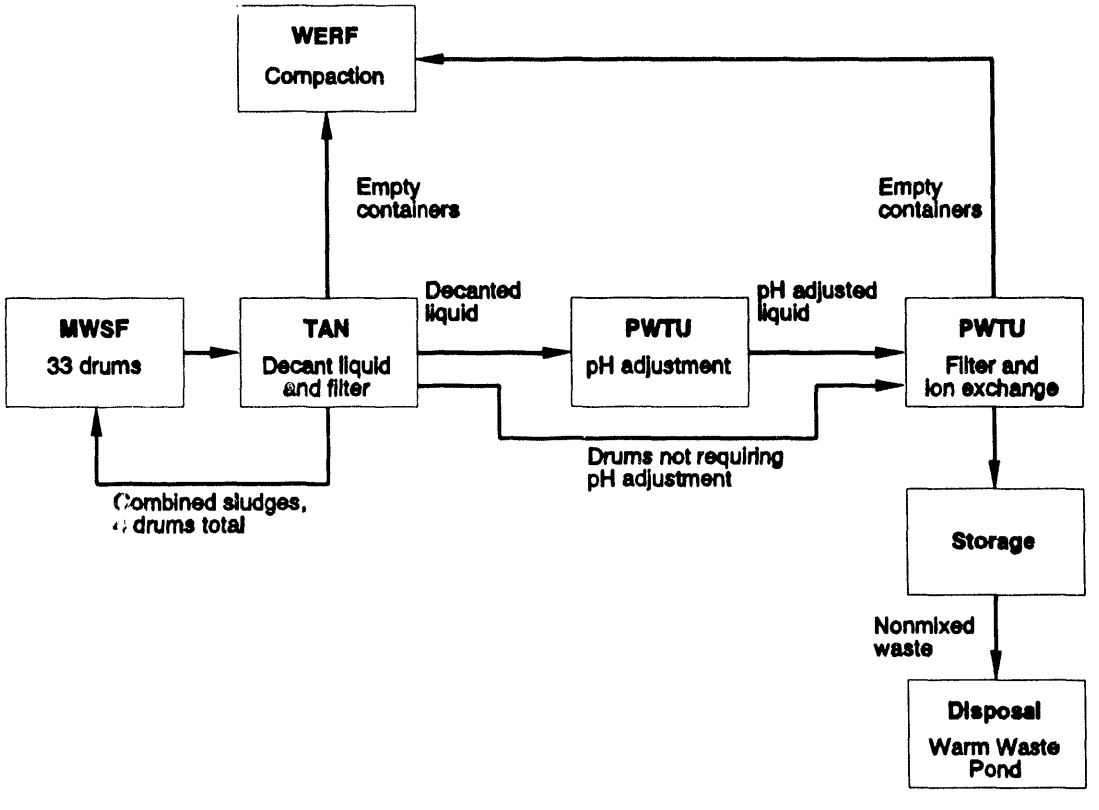

Figure 2. Process flow diagram for the treatment of TAN mercury-contaminated rinse solution.

Sludge Separation, pH Adjustment, and Ion Exchange, Trial 1

The processing of the waste entailed sludge separation at the TAN Hot Shop and pH adjustment and ion exchange at the PWTU. The details of processing the waste are in this section.

Sludge Separation at TAN. Sludge separation at TAN entailed the transporting of the waste to the TAN Hot Shop area, separation of the liquid from the solid sludge portion, and repackaging of the sludge for storage at the MWSF.

The liquid was separated from the sludge using a filter and pump assembly. The filtering system consisted of three series "L" Serfilco filter housings connected in series. Each filter housing accepts a 10-in., double-open-end filter. The first filter housing in the series had a 10-μ absolute rated filter installed. The second filter housing had a 1-μ absolute rated filter installed. The third filter housing had a 0.1-μ absolute rated filter installed. Pressure indicators on each filter housing provided indication that the filters were working and when the filters became depleted. An air-driven, Wilden diaphragm pump was used to pump the liquid out of the drums and force it through the filters. The diaphragm pump is a positive displacement pump and does not require priming. To ensure that the pump would not overpressurize the filter housings, the supply air was maintained at 65 psig, which is less than the 100 psig pressure rating for the filter system.

Waste drums were brought from the staging area into the Hot Shop in sets of four bound to a pallet. The pH of each drum was obtained and recorded (Table 1). The diaphragm pump was used to remove the liquid from the waste drums and pass it through the filtering system. The flexible inlet line to the pump was connected to a 4-ft length of 5/8-in. stainless steel tubing. The tubing was slowly lowered into the waste drum until the sludge phase was reached. Operators could identify the sludge by observing the fluid flowing through the clear tubing. Once the liquid was decanted to within 3–5 cm of the sludge phase, the suction line was placed into the next container.

Table 1 shows the drum numbers and information collected on each drum as the liquid was decanted. The liquid effluent from the filtering system ranged in colors from clear to brown. The pH of the effluent was also monitored for each drum. The filtered effluent was discharged into clean polyethylene drums. The drums were placed on a pallet and moved to the staging area at the TAN Hot Shop, and eventually to the PWTU.

The filters were replaced three times. The first time the filters were replaced when the discharge tube became stained with the waste in Drum 667. There was no sign of solid particulate passing through the filters, indicating that the solution was discolored from dissolved ions. The next two filter change-outs were performed when pressure readings across the filters indicated they were depleted.

After the liquid portion was removed from a set of four drums on a pallet, the sludge from these four drums was then consolidated into a 55-gal steel drum with a polyethylene liner. The sludge solution in the waste drum was mixed by using a small stainless steel propeller on the end of a 3-m-long shaft. A drill motor was used to drive the mixing shaft and propeller. The sludge was mixed with the 3-5 cm liquid layer that was left during the decanting stage to suspend the solid particulate. The mixed sludge solution was then pumped out of the drum and into the sludge accumulation drum. The sludge accumulation drums were filled about two-thirds full. The extra space was left in the drums to provide room to add a solidification agent for future solidification of the sludge. Four sludge accumulation drums were used. Table 1 indicates which sludge from each drum went into each accumulation drum.

Table 1. Drums filtered at the TAN Hot Shop and treated at the PWTU.

Drum number	Sampled prior to treatment	pH	Sludge placed in drum number	Drum number	Sampled prior to treatment	pH	Sludge placed in drum number
564[a]	No	9	4	626	No	10	3
565	No	9	3	627	No	10	3
568	Yes	11	1	630	No	10	3
569	No	8	1	635	Yes	7	1
570	No	9	1	636	No	9	1
571[a]	No	9	4	637	No	9	1
572[a]	Yes	8	4	638	No	7	1
575[a]	No	9	4	666	No	10	2
576[a]	No	11	4	667[ab]	No	9	2
587	No	7	3	668	No	10	2
588[a]	No	10	3	669	No	10	2
589	No	10	3	697	Yes	11	1
590[c]	No	9	4	700	No	3	No sludge
609[a]	No	9	3	701	No	3	3
610	No	7	3	702	Yes	3	No sludge
611	No	6	3	703	Yes	6	3
612[a]	No	11	2				

a. The solution in these drums had a brown color after filtering down to 0.1 μ. The remaining drums had a clear solution after filtering.
b. Drum 667 had 20–25 cm of sludge. Most of the drums had 5–7.5 cm of sludge.
c. Drum 590 had 15–20 cm sludge. Sludge was very thick and damaged the pump. Water was mixed into the sludge as a thinner. The pump was replaced.

After the sludge accumulation drums sat overnight, an attempt was made to decant excess liquid from these drums. However, the operators were unable to distinguish the sludge phase from the liquid phase and no water was removed.

After all the sludge had been removed, the empty drums were left bound to the pallets and prepared for shipment to the Waste Experimental Reduction Facility (WERF) for compaction. After compaction, the waste containers will be disposed of at the radioactive waste burial grounds at the INEL.

Adjustment of pH at the PWTU. The PWTU has a pH operating range of 6−9. The scoping studies indicated that the pH would drop 1−2 points in the ion exchange columns. Therefore, to stay above the pH limit of 6, the incoming waste had to be at a pH of 7-8.

Once at the PWTU, the drums were opened one drum at a time. The pH of the waste in each drum was measured and compared to the pH measured during sludge separation. Also, a 150−200 mL sample of the waste in each drum was transferred to a 30-gal drum to produce a composite mixture of all the waste. The composite mixture was sampled, and the sample was sent to Twin City Testing (TCT) for analysis. After the sample was obtained, acid or caustic was added to each drum as required to adjust the pH to 7−8. Note that TCT has been audited by EG&G Idaho and meets the requirements for an EPA Lab Program for quality assurance and quality control.

As can be seen in Table 1, two of the drums had a pH of 8, four of the drums had a pH of 7, and two of the drums had a pH of 6. No pH adjustment was made to these drums. Three of the drums had a pH of 3 and a 50% sodium hydroxide solution was added to these drums to raise the pH to 7−8. The remaining 22 drums had pHs of 9−11. Nitric acid was added to these drums to lower the pH to 7−8.

Originally, it was anticipated that as nitric acid was added, no precipitation would develop. However, as the acid was added, a precipitate did form. This precipitate was not analyzed because it was not thought to be mercury or lead because both of these compounds should have increased solubility in acid.

Filtering and Ion Exchange in the PWTU, Trial 1. The existing resin columns in the PWTU contain a general cation exchanger. This resin would not be effective at removing mercury to levels below the 0.2 mg/L RCRA limit. To ensure effective mercury and lead removal, heavy metal ion specific resins were used.

The amount of resin required to treat the wastewater was about $5.6 \times 10^{-3} m^3$ of GT-73. However, with this amount, the flow rate could only be $5.2 \times 10^{-2} m^3/h$. This flow rate would result in an unacceptable operating time, therefore, to decrease operating time, the flow rate was increased by using an excess of resin. Two resin columns were purchased, each with a $1.4 \times 10^{-2} m^3$ bed volume, giving a total bed volume of $2.8 \times 10^{-2} m^3$. This bed volume permitted a flow rate of 0.27 m^3/h, which required three days to process the waste. Processing time could be further reduced by increasing the resin capacity, but at the expense of generating more radioactive resin waste.

Once the columns were packed with resin, they were installed into a bypass line around the activated carbon beds. The activated carbon beds were not usable while the columns were installed.

Once a drum of waste on a pallet had the pH adjusted to 7−8, the solution was pumped from the drum using a peristaltic pump. The solution was pumped from the drums at a rate of 0.27 m^3/h as measured on the two flow meters/totalizers in the process trailer. The waste was fed to the inlet of the PWTU shown in Fig 1. The solution passed through 20-μ filters and then into the heavy metals ion exchange columns. Originally, the waste was fed through the general cationic ion exchange columns to remove the radioactive isotopes. However, the solution became very acidic in these columns. It was decided to bypass these columns and only go through the temporary heavy metal removal columns. After the waste was completely treated in the heavy metal columns, the waste was then processed through the general cation exchange resin to remove the radioactive isotopes. The treated waste was discharged to two tanks, each containing about 3.4 m^3.

The pressure drop across the temporary heavy metal columns slowly increased during processing. When the inlet pressure reached about 40 psig, the system was shut down and the first column was dismantled. Examination of the resin indicated that precipitated material formed during pH adjustment was passing through the 20-μ filters and collecting in the ion exchange columns, causing the columns to restrict the flow. The resin in the first column was removed and replaced with fresh resin. The system continued operation until about five drums remained, at which time the columns again became too plugged to continue operations. Both columns were then back flushed. After back flushing, the remaining drums of waste were treated.

After all the waste had been processed through the temporary heavy metal ion exchange columns, the PWTU was reconfigured so wastewater would flow through the three C-100H general cation, ion exchange resin columns. The wastewater in the two tanks was then reprocessed in the PWTU at the system design flow rate of 1.8 m^3/h. The wastewater had to pass through the activated carbon beds to bypass the temporary heavy metal ion exchange columns. As the waste was processed through the C-100H ion exchange columns, the pH of the waste dropped to less than 3, and the in-line automatic pH adjustment unit could not increase the pH. The treated solution in the tanks was cloudy, indicating precipitation was in the tanks. The bulk solution in the tanks was at a pH of less than 3. The solution was neutralized in the tanks. A pump was connected to recycle the solution in the tanks at about 140 gpm. Solid sodium hydroxide was then slowly added to increase the pH. As the sodium hydroxide was added, a precipitate formed. The final pH of the solution was at 9. The precipitate was not analyzed, but was assumed to be aluminum or sodium, both of which may pass through the resin columns.

Sampling and Analysis Results of pH Adjustment and Ion Exchange, Trial 1. Samples of the treated wastewater were obtained for radioactive analysis at the Radiation Measurements Laboratory (RML) located at the INEL, and were analyzed for TCLP metals, TCLP pesticides, and TCLP herbicides at TCT. A sample was also sent to the Environmental Chemistry Unit (ECU) lab located at the INEL for total RCRA-regulated metals screen. Gamma-ray results are shown in Table 2. TCLP test results from TCT are summarized in Table 3. Table 3 also shows the results of TCLP metals testing from ECU. The results are divided into Tanks 1 and 2, because the waste was placed into two tanks after treatment.

Table 2. Radioactive contamination of consolidated sample of treated liquid waste.

Waste form	Activity by isotope (pCi/mL)		Total activity (pCi/mL)
Untreated consolidated liquid (180–200 mL collected from each waste drum after filtration)	^{60}Co	2.10 ± 0.03 E+0	2.10 ± 0.03 E+0
Treated liquid, Tank 1[a]	^{60}Co	5.2 ± 0.5 E–2	2.11 ± 0.07 E–1
	^{137}Cs	1.59 ± 0.07 E–1	
Treated liquid, Tank 2[a]	^{60}Co	5.1 ± 0.5 E–2	2.82 ± 0.08 E–1
	^{60}Cs	2.31 ± 0.08 E–1	
Treated liquid, Tanks 1 and 2	^{60}Co	4.6 ± 0.5 E–2	2.69 ± 0.08 E–1
	^{137}Cs	2.23 ± 0.08 E–1	

a. The waste originally contained in 33 drums was discharged to two storage tanks from the PWTU.

Table 3. Mercury and lead concentrations of untreated waste and treated waste after each trial.

Treatment	Mercury TCT/ECU[a] (mg/L)		Lead TCT/ECU[a] (mg/L)	
Untreated consolidated liquid (180 to 200 mL collected from each waste drum after filtration)	7.000[b]		2.780[b]	
	Tank 1[c]	Tank 2[c]	Tank 1[c]	Tank 2[c]
Treated liquid Trial 1 (filtered to 20 μ then passed through S-920, GT-73, and C-100H resins)	0.264/ 1.900	0.0087/ 0.882	0.022/ 0.150	0.104/ 0.240
Treated liquid Trial 2 (Filtered to 0.1 μ, no ion exchange)	0.864/ 1.380[d]	1.788/ 1.380[d]	No data collected	No data collected
Treated liquid Trial 3 (filtered to 0.3 μ then passed through S-920 resin)	0.0092/ 0.0156	0.0168/ 0.033	No data collected	No data collected

a. TCT - Twin City Testing Corporation.
ECU - Environmental Chemistry Unit lab at the INEL.

b. These are TCT lab results only; a sample of the untreated consolidated liquid was not sent to ECU for analysis.

c. The waste originally contained in 33 drums was discharged to two storage tanks from the PWTU. The samples were labeled Storage Tank 1 or 2, but Tanks 1 and 2 are not necessarily the same storage tanks between processing trials.

d. Sample sent to ECU lab was a mixture of approximately equal amounts from each tank.

As can be seen by the results in Table 2, the original waste had a total activity of 2.1 pCi/mL. This is from a sample of the consolidated liquid representing the bulk waste. After treatment, the total activity was reduced to 0.269 pCi/mL. The original waste contained only ^{60}Co; however, after treatment the waste stream registered the presence of ^{137}Cs. The ^{60}Co was reduced to 0.046 pCi/mL, but the ^{137}Cs increased 0.223 pCi/mL, accounting for the majority of the radioactivity in the final waste solution. The cesium probably was removed from the resin columns in the PWTU. Cesium is an ion that is very difficult to remove by ion exchange. When the waste that contained a great deal of calcium and sodium ions was run through the ion exchange resin that had radioactive cesium already loaded on, the calcium and possibly some of the sodium replace the radioactive cesium on the active site of the resin, releasing the cesium to the wastewater solution.

Table 3 shows the mercury and lead results from TCT and ECU. The first metal results from ECU indicated that the mercury levels were reduced from 7.0 mg/L to an average of 1.39 mg/L, which is greater than the 0.2 mg/L RCRA limit. There was a large difference in values from Tank 1 at 1.9 mg/L to Tank 2 at 0.882 mg/L. Results from TCT arrived about a week later, and indicated that the mercury was barely above the RCRA limit in Tank 1 at 0.264 mg/L and well below the RCRA limit in Tank 2 at 0.0087 mg/L.

Table 3 shows the bulk lead concentration of 2.78 mg/L, which is less than the RCRA limit of 5.0 mg/L. Results from ECU indicate that lead levels were reduced to an average of 0.195 mg/L. Results from TCT indicate that lead levels were reduced to an average of 0.063 mg/L.

As can be seen in Table 3, there is a large discrepancy between ECU's and TCT's results. The analysis methods of TCT and ECU were compared to evaluate why there was such a large discrepancy between the two labs' results. It was evaluated that ECU was not following RCRA requirements for testing. ECU was acidifying the sample and then filtering, while TCT was filtering the sample and then doing the acid digestion. As a result, TCT was removing solid mercury compounds such as mercury oxide with the filtering, while ECU was putting the solid mercury into solution by acidification. This consistently produced higher metal results from ECU.

An evaluation was made to determine what may have caused the treatment to fail at reducing the mercury to RCRA limits, and what could be done to successfully process the waste. Three scenarios were identified that may account for the presence of the mercury in the treated wastewater. The first possibility was that the precipitated material from the three acidic drums contained mercury oxides, and insufficient filtration then allowed the mercury compounds to remain in the waste stream after treatment. The second possibility was that the precipitated material that lodged in the resin columns also plugged the active sites on the resin, making the resin ineffective. The third possibility was that the resin was not effective at removing the mercury ions. Of these three possibilities, it was believed that the first one was the most likely scenario. To help evaluate which scenario occurred, the remaining liquid sample that was taken for ECU analysis was filtered with a 0.45-μ filter and reanalyzed. The filtering of the sample lowered the mercury level to 0.025 mg/L, which is below the RCRA limit, indicating that solid particulate is responsible for the high mercury content.

Reprocessing by Filtration, Trial 2

This section details the steps taken to filter the waste treated in Trial 1.

Reprocessing by Filtration, Trial 2. After verification that filtering the sample was an effective treatment, a method to filter the wastewater was developed. The filtering unit originally used during the separation of the liquid from the sludge was installed in the PWTU. The last two filter housings were used and were plumbed to the system the same way the temporary ion exchange columns were installed. Also, 0.3-μ filters were purchased and installed into the permanent filter housings in the PWTU. The two temporary filter housings were fitted with 0.1-μ filters. The end result was that the waste was filtered through 0.3-μ filters, then into a 0.1-μ filter, and finally into another 0.1-μ filter. The activated carbon beds and the radioactive ion exchange columns were bypassed. The only treatment performed was filtration.

The waste was filtered through the system at a flow rate of about 1.4 m^3/h. There was about 2 cm of sludge at the bottom of the tanks. The sludge was not very compact and was easily suspended. The waste in both tanks was filtered down to a few inches above the sludge, so as not to stir up the sludge and require frequent filter changes during processing. After the liquid was removed from both tanks down to within a few inches of the sludge, the suction line was lowered into the sludge and the sludge was suspended. All the waste in both tanks was removed and the sludge material collected on the filters. The tanks were thoroughly rinsed with water and the rinse water was filtered. The filtered waste was discharged from the system to two polyethylene tanks. The 0.3-μ filters required seven change-outs to process the liquid, resulting in use of 14 filters. The first 0.1-μ filter in the series had to be changed out once. The second 0.1-μ filter did not require any change-outs. Upon dismantling of the filter system after all the waste was filtered, a very fine black precipitate was observed on the last 0.1-μ filter. The 0.3-μ filters collected about 90–99% of the particulate. The sludge on these filters looked like caramel (because of algae growth in

the tanks). The sludge on the two 0.1-μ filters that were removed from the second housing was black. The discharge liquid from the PWTU was very clear.

Prior to the start of filtering, the pH of the waste in the tanks was measured at 6, which is 3 points less then the pH of 9 that was measured one week earlier when Trial 1 treatment took place. Therefore, in a period of about a week, the pH of the waste in both tanks went from 9 down to 6.

Sampling and Analysis Results of Filtration, Trial 2. The sampling and analysis results of Trial 2 wastewater are shown in Table 3. Because sampling and analysis results from Trial 1 indicate that there are no TCLP pesticides, TCLP herbicides, and volatile organics, and because mercury was the only RCRA-regulated metal identified in the waste, the filter-treated wastewater was analyzed for mercury only. Samples were sent to both the ECU and TCT labs. The sample sent to ECU was an equal mixture of waste from both tanks. Samples from each tank were sent to TCT. The first results were obtained from ECU, but because of the large discrepancy between the two labs' results in the previous trial, it was decided to wait until TCT's results arrived before taking any action. As can be seen in Table 3, the results from both labs are very close. The average value for the two tanks from TCT is 1.326 mg/L. The result from the mixed solution from ECU is 1.380 mg/L. The values indicate that not only is the waste above the RCRA limit of 0.2 mg/L, but that the average concentration of mercury in the waste increased from the Trial 1 treatment.

The increase in mercury in the solution is assumed to have come from an equilibrium adjustment of the waste as it sat for a week between Trial 1 and Trial 2 processing. During this equilibrium adjustment, a precipitated mercury complex that went through the 20-μ filters and the resin columns probably went back into solution. There are three pieces of evidence to support this theory. First, the pH of the solution went from 9 down to 6 while sitting in the tanks for a week; this can only occur if ions either go into or out of solution. Second, the filtering of the ECU sample while still at a pH of 9 indicated that filtering would remove the mercury. Third, ECU results and TCT results were very close, indicating that the mercury was in solution when the samples were taken.

Reprocessing by Filtering and Ion Exchange, Trial 3

Analysis of the data from ECU and TCT showing high levels of mercury, combined with the fact that the liquid waste has been thoroughly filtered and is free of solids, indicates that the mercury is in solution. Because the treatability studies demonstrated that the ion exchange with S-920 works, it was decided to run the waste through the heavy metal ion exchange columns for a second time. In conjunction with this, the waste would be filtered through 0.3-μ filters.

Reprocessing by Filtering and Ion Exchange, Trial 3. The old resin in the two temporary columns was removed and placed into a drum. New S-920 resin was then packed into the resin columns. The temporary columns were plumbed into the system as they were in Trial 1. The permanent filter housings in the PWTU were fitted with 0.3-μ filters. The waste was processed at a flow rate of 0.27 m^3/h. The activated carbon beds and the radioactive ion exchange columns were bypassed.

During processing of the waste, there was no pressure increase on the ion exchange columns. Also, there was very little pressure increase on the filters and only one set of filters was required to process all the waste. The tanks were thoroughly rinsed with clean water, and this rinse solution was processed through the PWTU. The discharge came out clear. The waste was discharged to two polyethylene tanks that were identical to the ones used previously. When the filters were removed, they were coated with a green brown algae material. The resin in the columns showed no sign of sludge accumulation.

Sampling and Analysis Results of Filtering and Ion Exchange, Trial 3. The sampling and analysis results of Trial 3 are shown in Table 3. Again, only mercury was analyzed. The results from both labs indicate that mercury is below the RCRA limit. The highest values are from ECU at 0.0156 mg/L and 0.033 mg/L, respectively. The values from TCT are roughly half ECU values at 0.00919 mg/L and 0.0186 mg/L, respectively. These values are higher than the 0.0056 mg/L obtained from the treatability studies.

Wastewater Disposal. The wastewater was ultimately disposed of by discharging to the TAN waste pond TSF-07. The final volume of solution treated was about 7.5 m^3. This includes the original 6.8 m^3 of waste plus about 0.7 m^3 of water used to rinse the storage tanks and lines.

Sampling and Analysis of Filters and Resins

In the process of treating the TAN mercury-contaminated rinse solution waste, several components became contaminated with radioactive and hazardous waste. The resin columns and the pump and filter unit will be saved and used to treat wastes in the future. The depleted filters and the resins used in the temporary heavy metal ion exchange columns were placed into drums. The filters and the resins were sampled to determine if they were a mixed waste or a radioactive waste only. The results of the sampling and analysis of the filters and resin are detailed below.

Sampling and Analysis Results of Filters. A total of 32 filters were used in the processing of the TAN mercury-contaminated rinse solution wastewater. Of these 32 filters, 12 of the dirtiest filters were sampled. The filters were sampled following the procedures in the PWTU sampling and analysis plan, which includes a section for filter sampling. A knife was used to cut a 15 x 20-cm section of the filtering material off of the filter support. This was then cut into three strips; then each strip was placed into one of three containers. This was repeated for each of the 12 filters that were sampled, resulting in a strip from all 12 filters being combined to produce three composite samples. The composite samples were sent to TCT to be analyzed for TCLP metals, TCLP pesticides, TCLP herbicides, TCLP volatiles, and corrosivity. A sample was also sent to RML for gamma-ray analysis. Table 4 shows the mercury and lead TCLP results. The filters failed to meet the RCRA limit for both lead and mercury. The filters passed on all the other metals and no volatiles, pesticides, or herbicides were detected. Samples of the original sludge passed TCLP mercury, but failed TCLP lead. The reason that the sludge collected on the filters did not pass TCLP mercury is probably because of the generation of mercury oxide or other mercury complex during pH adjustment.

Table 4. Mercury, lead, and chromium TCLP and corrosivity results from TCT.

Waste form	Mercury (mg/L)	Lead (mg/L)	Chromium (mg/L)	Corrosivity (mm/yr)
Resin Sample 1	2.1	141	0.141	2.6 E−4
Resin Sample 2	2.74	3.12	0.14	4.5 E−4
Filters Sample 1	3.64	329	0.983	1.8 E−4
Filters Sample 2	1.55	344	2.21	2.1 E−4

Table 5 shows the activity of the sludge collected on the filters. Most of the activity is from ^{60}Co, with an average activity of 235 pCi/g. This activity was expected to collect in the filters because the treatability studies demonstrated that most of the activity was concentrated in the sludge.

Table 5. Radioactive contamination in ion exchange resin and filters.

Waste form		Activity (pCi/g)	Total activity (pCi/g)
Resins (sampled from columns)	^{60}Co	2.64 ± 0.03 E+2	2.65 ± 0.03 E+2
	$^{108}Ag_m$	10.00 ± 0.08 E−1	
Resins (sampled from drum)	^{60}Co	2.69 ± 0.04 E+2	2.7 ± 0.04 E+2
	$^{108}Ag_m$	9.90 ± 0.07 E−1	
Filters	^{60}Co	2.19 ± 0.03 E+2	2.29 ± 0.03 E+2
	$^{108}Ag_m$	2.48 ± 0.04 E+0	
	^{137}Cs	7.26 ± 0.16 E+0	
	^{152}Eu	6.30 ± 0.70 E−1	
Filters	^{60}Co	2.31 ± 0.03 E+2	2.42 ± 0.03 E+2
	$^{108}Ag_m$	2.81 ± 0.05 E+0	
	^{137}Cs	8.16 ± 0.11 E+0	
	^{152}Eu	6.40 ± 0.70 E−1	

Sampling and Analysis Results of Resins. A total of about $3.7 \times 10^{-2} m^3$ of resin was used in the Trial 1 processing. The resins were sampled following the PWTU sampling and analysis plan. The resin was placed into a drum, thoroughly mixed, and then a scoop was used to take the samples. This produced a composite sample of the resin used in Trial 1. The resin used in Trial 3 processing was added to this waste container after the sampling and analysis. Some of the samples were sent to TCT to be analyzed for TCLP metals, TCLP pesticides, TCLP herbicides, TCLP volatiles, and corrosivity. A sample was also sent to RML for gamma-ray analysis. Table 4 shows the mercury and lead TCLP results. As can be seen, the resin failed to meet the RCRA limits for both lead and mercury. The resin passed on all the other metals and no volatiles, pesticides, or herbicides were detected.

Table 5 shows the activity of the resin. Most of the activity is from ^{60}Co, with an average activity of 270 pCi/g. This activity is assumed to come from the solid particulate that collected in the resin. The activity is also due in small part to the cobalt and silver ions being removed from solution onto the resin.

The resins used in the treatability studies were tested for TCLP metals. This resin passed TCLP tests. This indicates that the sludge material that passed through the filtering system and became entrained in the resin resulted in the failure for the resin used to treat the bulk waste to pass TCLP.

CONCLUSIONS

Initial separation of the liquid from the solid portion of the waste using the pump and filter system described in this report worked very well. This system was also effective at pumping the sludge slurry to consolidate the sludge in the 33 original waste containers to four drums. The filter housings are designed to replace the filter without draining the housings by removing the top of the housing. However, placing the filters

into these housings and ensuring a proper seal between the filter and housing was very difficult because the filters would float in the wastewater.

Adjustment of pH of the waste in the drums is slow, poses several hazards, and should not be considered for normal operations. The addition of the acid in 10-mL increments through a pipet required a great deal of operator interaction with the concentrated nitric acid. Manual stirring of the waste with a stirring rod between each acid addition required a great deal of labor and increased the potential for spills and splashing.

The unexpected amount of precipitation produced during pH adjustment and the inadequate filtering by the 20-μ filters resulted in particulate reaching the resins and the treated waste storage tanks. It is likely that the addition of sodium hydroxide to the three acidic drums produced mercury oxide or possibly a mercury complex that passed through the filtration system and the resin columns, and resulted in the failure of the Trial 1 treatment to reduce mercury concentrations to the required levels.

The filtering of the waste in Trial 2 treatment was ineffective. The pH of the waste had decreased from 9 to 6. This probably resulted in the mercury oxide or a mercury complex dissolving into solution, making filtration ineffective. The sample of the Trial 1 treated waste did not undergo the same spontaneous pH change, probably because an insufficient amount of precipitated material was in the sample to allow the same equilibrium reaction to occur.

The ion exchange treatment with proper filtration of the waste in Trial 3 effectively treated the waste and reduced the mercury levels to 0.0186 mg/L. The S-920 resin is an effective resin to reduce mercury levels to less than the RCRA limit of 0.2 mg/L, but may not be capable of attaining drinking water standards of 0.002 mg/L.

The final liquid waste solution was below the RCRA limit for mercury at less than 0.0186 mg/L and for lead at less than 0.240 mg/L. Radioactivity levels were less than 0.282 pCi/mL, which is less than the derived concentration guideline (DCG) values for ^{137}Cs and ^{60}Co at 3 pCi/mL and 5 pCi/mL, respectively.

The filters produced from this process are a mixed waste. Ultimate disposal will probably be incineration at WERF.

The solid particulate matter did not appear to affect the resin's ability to remove dissolved mercury and lead ions because there was a definite decrease between the concentrations of the treated waste over the nontreated waste. However, the solid particulate matter that was entrained in the resin resulted in the resin's failure to pass TCLP. It is likely the resin from Trial 3 and future resins would pass TCLP if proper filtration were employed, because the resins in the treatability studies passed TCLP.

RECOMMENDATIONS

PWTU Changes

The treatment of the TAN mercury-contaminated rinse solution demonstrates that ion exchange is an effective treatment of mixed waste solutions containing dissolved ions. However, this treatment demonstration also pinpoints several deficiencies in the existing PWTU. The areas of concern that have been identified from the testing are:

- The inability to treat the waste at one location
- The hazards associated with pH adjustment of the waste while contained in the waste drum
- The limited acceptable pH range for wastes
- The inability of the pumping, piping, and filtration systems to handle very fine particulate
- The inability to allow increased resin capacity or addition of different resins without having to make piping changes to the system
- The inability of the system to adjust the pH of the treated waste prior to discharging the waste from the PWTU.

Each one of these concerns are addressed in detail below.

Permitting and Safety Documentation Changes. To perform the treatment of this waste, Part A of the RCRA permit had to be expanded to include waste codes D008 and D009 for lead and mercury, respectively. To continue processing mixed wastes, the PWTU permits must be modified. An evaluation must be performed to determine the hazardous materials in existing wastes at the INEL and the potential hazardous material that may be in future wastes. The RCRA and State permits should then be expanded to include the identified hazards. Also, the current safety documentation is very restrictive. To treat the TAN mercury-contaminated rinse solution, the sludge had to be removed at a separate location. This created the added hazard of transporting the waste from one location to another. An evaluation should be made of the PWTU SAR and hazard classification and compare this to wastes identified for potential treatment and future wastes that may be treated. Modifications should then be made to this documentation to ensure that the safety envelope covers as wide of a variety of wastes as possible.

pH Adjustment System Addition. For the purposes of demonstration testing, the pH adjustment of wastewater in the waste drum was acceptable. However, for regular day-to-day processing, this would not be an acceptable practice. To ensure the safe processing of future waste streams, a pH adjustment system is required. The pH adjustment system must be capable of neutralizing both acidic and caustic solutions. The system should be able to adjust the pH of the waste feed stream at a continuous flow rate that matches the processing rate of the rest of the system.

To ensure optimal performance from the resins, the system should be designed to accept a variety of wastes at a pH range of 1 – 13. An analysis should be performed of the system to ensure all wetted piping material is compatible with potential wastes and desired operating pH range.

Filtration Changes. The filtering and pumping systems should be expanded to include more capability to handle solids. The filtering system must be able to handle more solids and must be able to filter to less than 0.45 μ. To optimize filtering capability, the filtering system should consist of a series of two or more filtering assemblies. The filtering assemblies should have decreasing micron ratings with the last assembly in the series containing 0.45-μ filters or smaller. The first filtering assembly should be designed to remove 80 – 90% of the solids from the waste stream. A pumping system must be added that is capable of removing the waste from the containers and also pumping thick sludges for waste consolidation and minimization.

Resin Column Expansion. To add the temporary columns to the present system, the activated carbon beds could not be operated. To treat a variety of waste solutions containing many different dissolved ions, the system should be capable of adding on resin columns without having to make extensive piping changes or without removing processing capabilities.

Radioactive Resin Evaluation. The appearance of ^{137}Cs in the treated solution indicates that cesium was being removed from the C-100H resin. An evaluation should be performed to investigate the vendor information to determine if C-100H resin is the best resin to use for radioactive ion removal. At present, this resin has removed radioactive isotopes from waste streams to less than DCG levels and C-100H has passed TCLP testing.

Final pH Adjustment Changes. Currently, the neutralization system at the discharge of the PWTU is capable of neutralizing weak acidic or caustic solutions. However, if heavy ion exchange takes place, as it did in the treatment of this waste, and lowers the pH of the treated solution, the system is not able to neutralize the waste for disposal. A means should be provided to neutralize this waste, either by providing a more efficient system at the discharge or by reprocessing through a pH adjustment system at the inlet of the PWTU.

PWTU Recommendation Summary

The following changes should be made to the PWTU in order to process mixed wastes in a safe and effective manner.

Permitting and Safety Documentation. The permitting should be expanded and made as liberal as possible. The permitting should not only include current waste hazards at the INEL, but possible future waste hazards that will be created as decontamination and decommissioning (D&D) and site remediation functions expand at the INEL.

The safety documentation should be expanded and made as liberal as possible to include as many hazardous and radioactive wastes as possible.

Larger Trailer. The current PWTU has about 9 m^2 of area. At this time there is no room for expansion. To add on the capabilities of pH adjustment of the feed waste and the ability to add on resin columns requires the system to be installed into a larger PWTU trailer.

System Design Changes. The system installed into the larger PWTU trailer should contain the following systems at a minimum:

- Pumping system capable of removing wastewater and sludge from 55-gal waste drums.
- pH adjustment system capable of adjusting the pH of strong acidic and caustic solutions to a pH range of $1-13$.
- Piping system capable of handling strong acidic and caustic solutions containing 20% particulate by weight.
- Filtering system capable of removing a large quantity of fine particulate. The filtering system must be capable of removing particulate down to 0.45 μ.
- System must continue to have organic removal capabilities with activated carbon beds.
- System should continue to have three general cationic resin columns to remove radioactivity, followed by a column with resin specific for heavy metals. This should be followed by spare connections to add on columns loaded with ion specific resins for individual waste streams.
- Increased pH adjustment of the treated waste prior to final discharge from the PWTU. This system should be able to adjust the treated waste to a pH of $6-8$.

In addition to these changes, all existing features in the PWTU not mentioned here should be kept. No functions of the trailer should be eliminated when the process is transferred to a larger trailer.

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TREATABILITY STUDY FOR THE AMALGAMATION OF A RADIOACTIVELY CONTAMINATED ELEMENTAL MERCURY WASTE AT THE IDAHO NATIONAL ENGINEERING LABORATORY

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ABSTRACT. Treatability studies of radioactively contaminated elemental mercury were performed at the Idaho National Engineering Laboratory (INEL). The treatment that was used for this waste form was amalgamation, the treatment standard as defined by 40 CFR 268, "Land Disposal Restrictions." An investigation team performed initial tests with noncontaminated mercury in order to determine process conditions producing adequate amalgam forms. The team felt that the desired amalgam forms would have the following properties:

- The initial solid is a malleable mass
- Within 24 hours, this solid hardens into a nonmalleable one
- There is no free mercury on visual inspection
- There is no free mercury upon centrifuge testing.

In order to produce this waste form for the radioactively contaminated elemental mercury waste, a set format was determined. The metal of choice for amalgamation was -325 mesh copper. Steel balls (~4-mm diameter) were used to create a ball-milling effect for the powder. The amalgamations were performed in 250-mL widemouth high density polyethylene bottles, agitated by the use of wrist shakers. Five-minute pretreatments involving wrist shaking a mixture of 3.7 mL of 1 M nitric acid to approximately 79 g of copper and 78 steel balls. After pretreatment, about 102 g of mercury was added and the bottle was shaken for an additional 40 minutes to create amalgams having the aforementioned properties.

At the INEL, about 1.5 L of mercury waste was treated. A toxicity characteristic leaching procedure (TCLP) on the amalgam produced a leach extract having a below regulatory level of mercury (~0.0294 mg/L). As a result, the radioactively contaminated elemental mercury was both treated, per the amalgamation treatment, and nonhazardous, per the TCLP results. Upon verification of the TCLP results, the mercury amalgam is to be classified as a low-level waste, and is targeted for disposal at the Radioactive Waste Management Complex, a Subtitle D disposal facility. For radioactively contaminated elemental mercury, copper powder amalgamation can produce an amalgam that is nonhazardous and of a desirable physical form for disposal.

INTRODUCTION

At the Idaho National Engineering Laboratory (INEL), treatability studies were conducted to test treatments for radioactively contaminated elemental mercury. The treatment was to employed for elemental mercury radwaste that was in storage at the INEL. According to Table III of Land Disposal Restrictions the treatment standard for radioactive elemental mercury is amalgamation (1). When a treatment standard is

expressed as a specific technology and not a numerical figure, that specific technology must be performed in order for the waste to be considered treated for land disposal purposes. Deviations from that specific technology requires a treatment variance petition to the Environmental Protection Agency (EPA). Expected response from the EPA could take up to two years.

The purpose of this treatability study was to accomplish three main goals. The first goal was to test various parameters important to the amalgamation process. This was accomplished by using a representative model of the waste; specifically, commercial-grade elemental mercury. The second goal of the treatability study was to use an acceptable technique developed from the elemental mercury study and to confirm the procedure using actual waste. Since the waste was less than 1000 kg, all the waste could be treated in the treatability study. The third goal of the study was to create procedures that could be used for treatment of future contaminated mercury waste. The procedures could be used either directly or as a starting point for a scale-up treatability study.

This paper consists of a background discussion of Resource Conservation and Recovery Act (RCRA) regulatory issues concerning contaminated mercury, a background of the technology concerns of the amalgamation process, a discussion of the bench-scale activities and observations, and a recommendation for potential scale-up of the process.

AMALGAMATION BACKGROUND

In many amalgamation processes, the goal of amalgamation is to recover a desired metal, e.g., gold, by using mercury to separate the desired metal from the materials present by forming an amalgam. This amalgam is retorted, driving off the elemental mercury, and the desired metal is recovered. The main application for amalgamation in which properties of the amalgam form have significance is tooth restoration for the dental industry. Since tooth fillings reside in a person's mouth, the two properties of importance are that:

- The fillings should be fairly nonleachable, at least to saliva
- The fillings should not emit a significant amount of mercury vapors.

Given the information concerning amalgamation provided by the EPA, these two properties of dental amalgams should be the same properties that the EPA would also want from an amalgam. Based on this assumption, it was the goal of this research to achieve amalgams that would be fairly similar in form to tooth fillings. In the dental industry, amalgams are made with silver-tin alloys. The stoichiometric designation for the alloy is Ag_3Sn, representing a simplified description of the alloy material. Dental alloys are sold as commercial formulations, and can include metals such as copper, zinc, and mercury in the mixture. The compositions vary depending on the manufacturer.

In the present study, it was necessary to try to pick suitable metals/alloys for waste treatment. Since there were no strict physical requirements needed for the amalgams, the choice for potential metals was made based on four requirements: (a) metals must consist of a single component, i.e., no alloys; (b) metals must contain no toxic characteristic hazard; (c) metals must be relatively inexpensive; and (d) metals should have a fairly high mercury loading in amalgam form.

The potential metals that were considered for this investigation were narrowed to these choices: copper, gold, nickel, silver, tin, and zinc. All of these metals pass the first criteria of consisting of a single component, thereby reducing excess analysis caused by multicomponent alloy phases. Silver, although used extensively for tooth restorations, was excluded from this list because of its toxic characteristic designation (D011). Gold was excluded from this list because of its expense. Nickel was excluded because of its inability to amalgamate directly with mercury. The list was thus reduced to copper, tin, and zinc. In order to choose between these three metals, binary phase diagrams were used. The phase diagrams of mercury-copper, mercury-tin, and mercury-zinc are shown in Figures 1 through 3. As illustrated in these diagrams, only one phase exists at room temperature for all three binary systems. Based on these phase diagrams, Table 1 gives an indication of the minimum mercury amount needed, assuming equilibrium, for the intermetallic binary phase to be in equilibrium with the liquid metal phase, comprised mostly of mercury. Below these mercury levels, either the intermetallic phase exists by itself or is in equilibrium with a solid metal phase consisting mostly of the copper, tin, or zinc metals. Using the phase diagram as an indicator, the choice of metals was reduced to copper and zinc. Tin was excluded from the list because of the low percentage of mercury in the amalgam for the intermetallic binary phase to be in equilibrium with free mercury. Large quantities of tin would be required to treat a given amount of contaminated mercury, resulting in a large increase in the mass of disposable waste generated from a relatively small amount of mercury. It was not known at the start of the study whether or not the apparatus or approach employed to create an amalgam would be conducive to obtaining an equilibrium state for alloy formation within the amalgam. In order to determine the range of mercury dosages to use for either copper or zinc, trial and error in the laboratory would have to be employed for a given mixing scheme.

The particle sizes of copper and zinc that were chosen for this study were -325 mesh (<44 μm), -100 mesh (<150 μm), and -20 mesh (<841 μm). Dental alloys are typically below 50 μm in size (~22 μm mean); therefore, the -325 mesh particle size would best represent dental alloys.

A simple mixing system that could produce suitable amalgams was sought and then the other parameters, such as mercury dosage, were varied around this fixed mixing scheme. Through trial and error in the laboratory, processing time and mercury dosages were determined and fixed for all subsequent runs.

Table 1. Mercury content and mass increases for amalgams made with various metals.

Metal	Minimum mercury concentration required for free mercury to appear (%wt)	Mass increase at the minimum mercury concentration (%wt)
Zinc	57	75
Copper	76	30
Tin	19	430

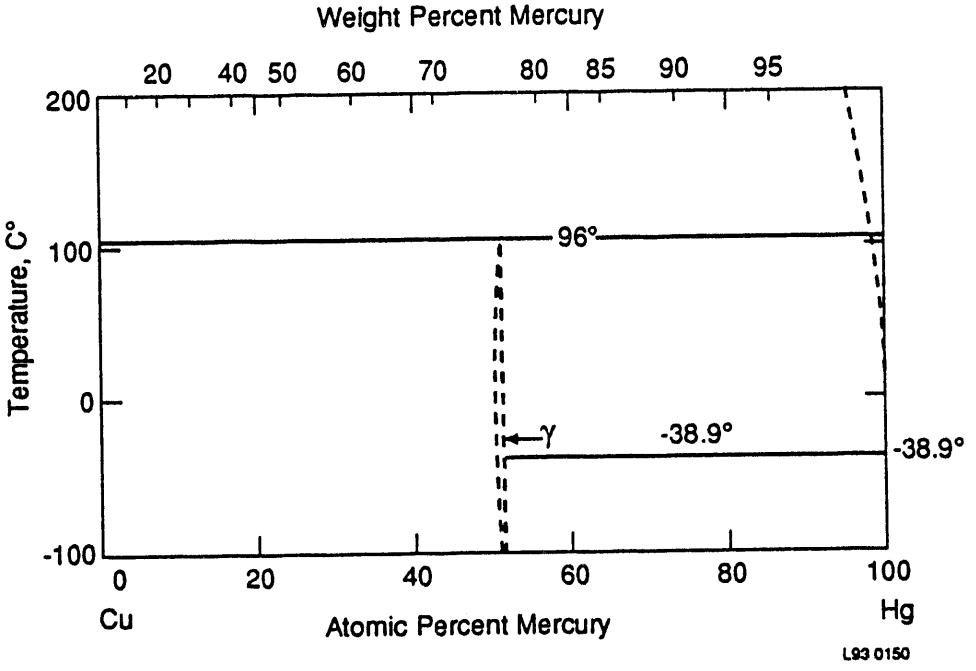

Figure 1. Binary phase diagram for mercury-copper (Ref. 2).

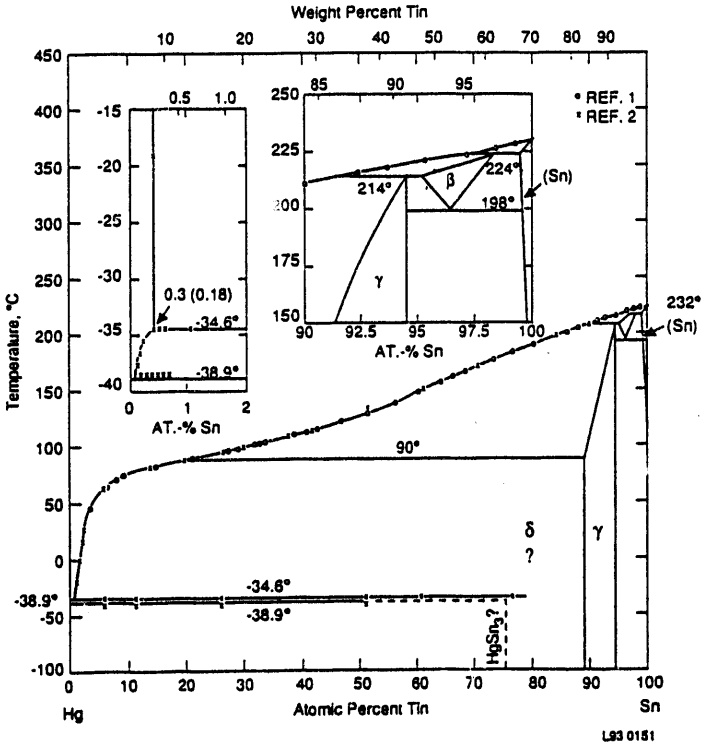

Figure 2. Binary phase diagram for mercury-tin (Ref. 2).

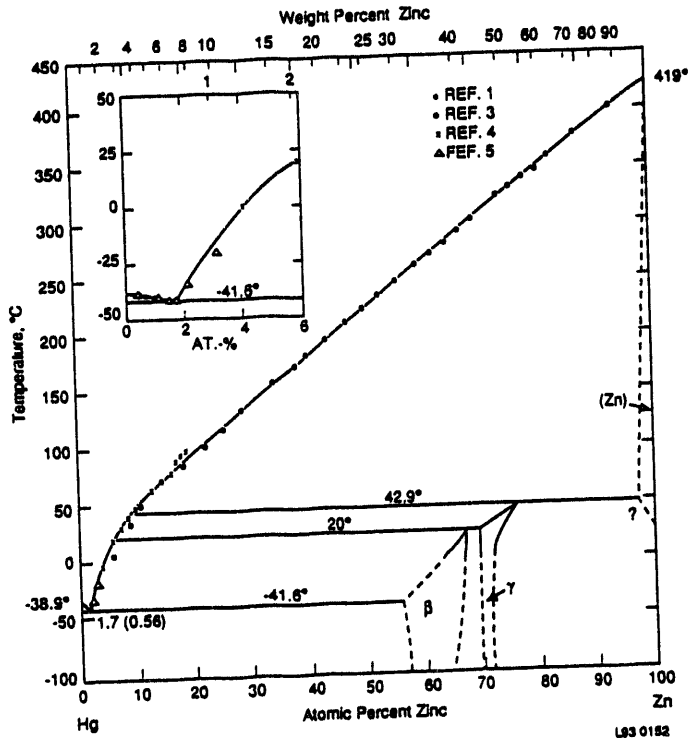

Figure 3. Binary phase diagram for mercury-zinc (Ref. 2).

EXPERIMENTAL

The experimental work performed on the noncontaminated mercury to achieve an acceptable amalgamation procedure progressed in two main phases; amalgamation with mercury in the form of aqueous ions and amalgamation with mercury in the elemental form. Specific procedures for the various sets of runs within these phases are presented in the discussion section of this report.

The mercury that was used for the nonradioactive phase of this study was tripled distilled from the National Zinc Co., Inc. As was stated previously, the metals that were used for this study were copper and zinc powders. The particle size of the powders were -100 and -325 mesh for both zinc and copper, and -20 mesh for zinc only. The powders were purchased from Atlantic Equipment Engineers Co. Nitric and hydrochloric acids (Fischer Scientific, Reagent A. C. S.) were used as pretreatment agents.

A Burrell Model 75 wrist-action shaker was used to mix the internal material of amalgamation bottles. The amalgam material was placed in a 60-mL high density polyethylene (HDPE) widemouth bottle for the small-scale cold studies and a 120-mL HPDE widemouth bottle for larger mixed waste processing. Steel balls (Mayville Engineering Co., Inc.) were used to assist in the amalgamation process. One fixed bed set-up required the use of a 25-mL buret with an inserted glass wool plug at the bottom. Another fixed bed set-up used a filter arrangement that used vacuum suction. The following materials and equipment were used in

this experimental study:

Types of metals:	Copper Zinc
Particle sizes:	-325 mesh (<44 μm) -100 mesh (<150 μm) -25 mesh (<841 μm)
Particle/mercury contact scheme:	Wrist shaker (aqueous or nonaqueous) Particle bed (aqueous) Ultrasonic bath
Mercury dosage (percent mercury):	To be determined
Acid pretreatment:	HNO_3 HCl.

DISCUSSION OF BENCH-SCALE PROCEDURES AND RESULTS

Initial amalgamation attempts were made with zinc and copper powder mixed directly with elemental mercury in a 60-mL container on the wrist shaker. The mercury did not interact with the powder, regardless of the length of time for mixing. As a result of the poor interaction, mercury was dissolved in an acidic solution prior to interaction with the powder. Nitric acid solutions were used due to the ease of dissolution. The mercuric solution was kept fairly acidic to keep mercuric nitrate precipitation from occurring. The mechanisms that allow for amalgamation under these conditions are:

$$Hg^{+2} + M_x(s) = M^{+2}(aq) + HgM_{x-1}(s) \quad (1)$$

$$Hg^{+2} + HgM_{x-1}(s) = M^{+2}(aq) + HgM_{x-2}(s) \quad (2)$$

where

M is either zinc or copper.

In this reaction, a mercury ion is reduced while a metal atom is oxidized. The metal (copper and zinc) is more easily oxidized than the mercury, as is shown by the following oxidation potentials:[4]

$$Zn = Zn^{+2} + 2e^- \qquad E^o = 0.7628\ eV \quad (3)$$

$$Cu = Cu^{+2} + 2e^- \qquad E^o = -0.3402\ eV \quad (4)$$

$$Hg = Hg^{+2} + 2e^- \qquad E^o = -0.851\ eV \quad (5)$$

Upon reduction, the mercury would be incorporated with nearby metal sites to form the amalgam. Mercury, possessing a lower oxidation potential than the powdered metal, should not come back out of the amalgam as ionic mercury. An advantage of wet amalgamation is that the mercury phase is present as dispersed ions

that nucleate onto metal sites. The aqueous phase is in excess of the solid phase with a low surface tension as compared to elemental mercury, and can flow to many different metal surfaces.

In an initial set of experiments, various mixing schemes were deployed. The mercury was introduced to the metal either as the elemental form or as solutions of varying acidities and concentrations. The metal powders were pre-washed in acid prior to the addition of mercury when introduced in its elemental form. The results of this initial set of experiments were to develop future series of experiments based on set mixing schemes and fixed procedures. The amalgamations in this series of tests were performed either in an open beaker within the fume hood or in an enclosed 60-mL HDPE bottle. In some cases, it was necessary to initiate acid solution contact with the metal in an open container because of gas liberation in the early stages of mixing. These observations were noted upon completion of this set of runs:

- The mercury/metal ratio in these runs to achieve amalgamation was around 10/90, representing a much lower ratio than anticipated, according to the phase diagrams
- Ultrasonic agitation was of no benefit to the amalgamation process as a post-mixing step. As seen in Figure 4, the mercury concentration in the aqueous solution increased as a result of mercury redissolving from amalgam structure.
- Amalgams formed from the interaction of dissolved mercury and metal powders contained less free mercury than amalgams formed from the interaction of elemental mercury and metal powders.
- A high (mercuric solution volume)/(metal weight) ratio formed better amalgams, illustrated through the poor amalgams of T7, T11, and T12, all of which were performed at low ratios.

A set of 15 experiments (nested design scheme) were set up to determine the effects of metal type, particle size, and mercury dose (mercury concentration in solution) on the amalgams resulting from bed amalgamation. In all of the runs listed in Table 2, 50 mL of mercuric solution was passed through 20 g of metal powder. A 10-mL portion of 1 M HNO_3 followed by two 10-mL portions of deionized water was passed through the column prior to passing through five 10-mL aliquots of mercuric solution. The column runs were initially to be performed in a 25-mL buret, utilizing either gravity or bulb suction to promote flow. It was determined that at smaller particle sizes, there would be much restrictive flow of the fluid due to packing of the small particles. Also, as the amalgam was being formed, there was a tendency for the amalgam to plug up flow. A second column, featuring filter capabilities, was chosen. A vacuum could be applied, thus allowing for the solution to be drawn through the particle bed. Also, as the amalgam was being formed at the top of the bed, the vacuum could be adjusted to keep the flow constant (1.4 mL/min). This filter bed arrangement had a bed that was 12 times shorter than the buret tube column for a given weight of metal powder.

There were some difficulties encountered with this bed arrangement:

- There were process control difficulties with respect to monitoring and maintaining constant flow
- There were difficulties in the initial loading of the powders into the bed to achieve optimal bed configuration
- As mercuric solution passed through the bed, chemical reactions (gas liberation) caused the bed to lift and shift around.

In all of the runs, the profiles of the amalgams through the bed were never more than one-third or one-half of the way down the bed. In some of the runs, elemental mercury was present in the amalgams. The top half of the bed was becoming effectively overdosed with mercury, resulting in the formation of elemental mercury in some of the runs. Elemental mercury formation was the result of the inability to incorporate the whole length of the bed in the amalgamation process. For a couple of trial runs, it seemed as though amalgam penetration through the bed was independent of flow rate, which is not the case for normal bed

processes. The top half of the bed in some instances continued to be overdosing with mercury. In some instances, it seemed as though the mercury was forming without incorporating into an amalgam form. The mechanism for elemental mercury formation from this solution process hinges on the pH effects. Some of the effluents were checked for pH and were found to have pHs of around 4.5, even though the incoming solution had a pH of less than 1. This rise in pH was probably due to some of the following reduction reactions:

$$NO_3^-(aq) + 3H^+(aq) + 2e^- = HNO_2(g) + H_2O \quad (6)$$

$$NO_3^-(aq) + 4H^+(aq) + 3e^- = NO(g) + 2H_2O \quad (7)$$

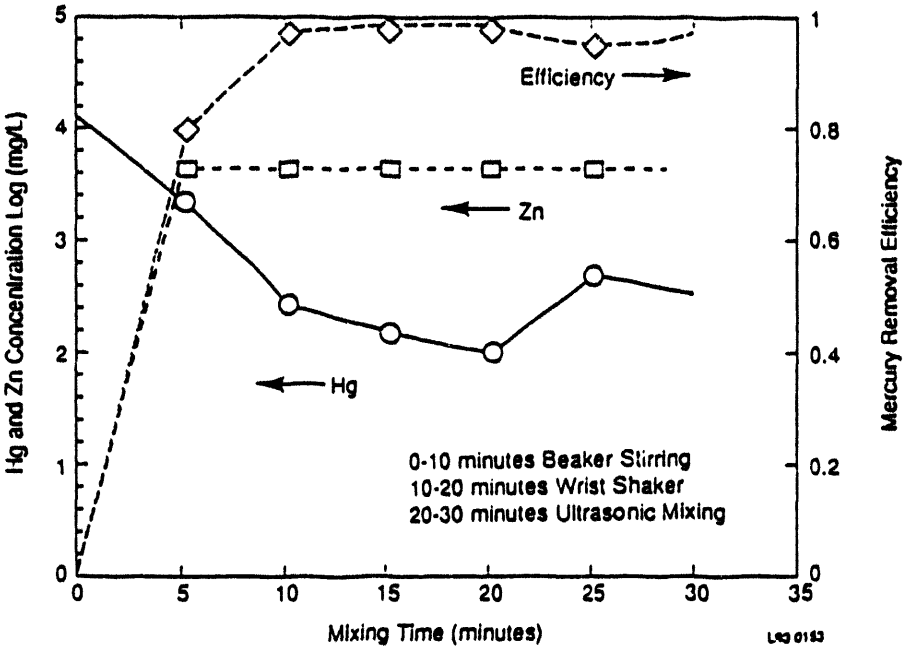

Figure 4. Solution concentrations for three-phase mixing amalgamation (Run T-9).

Table 2. Conditions for packed bed experiments.

Run number	Metal powder	Powder size	Mercury concentration, M	Free mercury classification[a]
R1	Zinc	-20 mesh	0.66	2–3
R2	Zinc	-20 mesh	0.22	1
R3	Copper	-100 mesh	1.33	3–4
R4	Copper	-100 mesh	0.22	1
R5	Zinc	-20 mesh	1.33	4
R6	Copper	-325 mesh	0.66	2–3
R7	Zinc	-100 mesh	1.33	4
R8	Copper	-325 mesh	0.22	1–2
R9	Zinc	-100 mesh	0.66	2–3
R10	Zinc	-100 mesh	0.66	2--3
R11	Zinc	-100 mesh	0.22	3
R12	Copper	-100 mesh	0.66	1–2
R13	Copper	-325 mesh	1.33	1–2
R14	Copper	-325 mesh	0.66	1–2
R15	Copper	-100 mesh	0.66	1–2

a. Key:
1. No free mercury is present in the amalgam.
2. Tiny droplets of mercury are dispersed through the amalgam.
3. Droplets of mercury are dispersed throughout the resultant amalgam.
4. Bulk amount of mercury is associated with the amalgam.

$$2NO_3^-(aq) + 4H^+(aq) + 2e^- = N_2O_4(g) + 2H_2O \quad (8)$$

$$2H^+(aq) + 2e^- = H_2(g) \quad (9)$$

In all of these reactions, the H^+ ion serves as a reactant. The accompanying oxidation reaction would be either simple oxidation of the base metals or oxidation of the amalgam, causing both pH changes and gas generation. Reactions (8) through (11) might cause the following oxidation to occur that accounts for the formation of elemental mercury:

$$HgM(s) = Hg(1) + M^{+2}(aq) + 2e^- \quad (10)$$

where

$$E^o = +0.7628\ eV\ for\ M = Zn \quad (11)$$

$$E^o = -0.3402\ eV\ for\ M = Cu\ . \quad (12)$$

One observation of the particle bed reactions was that there was far less free mercury involved with the copper bed than with the zinc bed. This was probably because of the ease of oxidation of the zinc relative to the copper, thus releasing more free mercury from the zinc amalgam rather than the copper amalgam. The two pieces of information that could be gathered from this series of experiments are:

- Copper is a better metal for amalgamation than zinc because of a more apparent vigorous reaction and less free mercury in the amalgams (comparing Runs R3, R4, R12, and R15 with Runs R7, R11, R9, and R10)
- The smaller particle size of copper is more effective in accumulating mercury, probably due to increased surface area (Fig. 5).

The equipment that dentists used in the past for making amalgams was a mortar and pestle. It was surmised that the pressing and grinding motion of the pestle against the mortar acted to crush oxide surfaces off of the powder and to squeeze the mercury into the powder. It was speculated that the pressing of the powder and mercury occurring between the mortar and pestle helped to thin out the mercury over more available copper surface, which became necessary because of the inherently high surface tension of the mercury. There were indications from a mortar and pestle trial in the lab that mercury and copper were truly forming an alloy. The absence of free mercury better reflected what was to be expected as shown through the phase diagram for copper-mercury (Fig. 1). A set of experiments were derived that could develop this method of amalgamation. The process required softening of the surfaces of powder using very small quantities of acid, with grinding balls acting as the pestle. The acid and balls are needed to remove oxide layers, inherent with metal powders exposed to air, from the surface of the copper. This oxide layer interferes with the ability of mercury to interact with the base metal, copper in this case, hindering amalgamation. The acid was deemed to soften the oxide layer, since copper oxide is soluble in acid:

$$2H_3O^+(aq) + CuO(s) = Cu^{+2}(aq) + 3H_2O\ . \quad (13)$$

The oxide layer corrodes off of the copper particles, thus allowing a fresh, unoxidized surface to be exposed. Powder, mercury, acid, and grinding balls would be added to a bottle, which would be wrist shaken. The grinding balls would act to knock off oxide surfaces and to squeeze/spread the mercury onto the copper surfaces. A set of experiments was devised to test amalgamation using grinding balls, and is shown in Table 3. Copper powder at a size of -325 mesh was chosen for this set of experiments based on the conclusions derived from the packed bed experiments. The procedures for this set of experiments were as follows:

1. Copper powder (-325 mesh), a small amount of acid, and steel balls were placed in a polyethylene bottle and shaken for five minutes

2. Mercury was added to the bottle, and the composite was shaken for 40 minutes.

Table 3 gives the quantities of material that were needed for each of the runs that correlate to the aforementioned procedures. A summary of the various runs follows:

Table 3. Conditions for ball milling amalgamation

Run number	Mercury dosage (%)	Pretreatment acid	Volume of pretreatment acid	Number of grinding balls	Mass of -325 mesh copper (g)
L1	50.0	Nitric, 1 M	25 mL (filtered)	10[a]	19.44
L2	33.3	Nitric, 1 M	25 mL (filtered)	10[a]	21.32
L3	20.0	Nitric, 1 M	25 mL (filtered)	10[a]	22.44
L4	50.0	None	0	20[a]	20.00
L5	50.0	None	0	20[b]	24.00
L6	57.1	None	0	22[b]	20.16
L7	56.2	Nitric, 1 M	1.0 mL	20[b]	20.35
L8	56.5	Deionized water	1.0 mL	20[b]	20.86
L9	56.2	Nitric, 1 M	1.0 mL	20[b]	20.73
L10	50.2	Nitric, 1 M	1.0 mL	20[b]	20.50
L11	53.1	Nitric, 1 M	1.0 mL	20[b]	20.54
L12	53.0	None	0	20[c]	20.42
L13	53.0	Nitric, 1 M	0.2 mL	20[c]	20.48
L14	53.0	Nitric, 1 M	0.5 mL	20[c]	20.53
L15	53.0	Nitric, 1 M	1.0 mL	20[c]	20.77
L16	56.2	Nitric, 1 M	1.0 mL	20[c]	21.60
L17	56.2	None	0	20[c]	21.55
L18	56.2	Nitric, 1 M	0.2 mL	20[c]	21.49
L19	56.2	Nitric, 1 M	0.5 mL	20[c]	21.07
L20	56.2	Nitric, 1 M	3.5 mL	83[c]	75.85
L21	56.2	Nitric, 1 M	0.8 mL	17[c]	16.55
L22	56.2	Nitric, 1 M	3.4 mL	71[c]	72.26
L23	56.2	Hydrochloric, 1 M	1.0 mL	20[c]	20.68
L24	59.6	Hydrochloric, 1 M	1.1 mL	22[c]	22.03
L25	65.0	Hydrochloric, 1 M	1.0 mL	20[c]	20.53
L26	70.0	Hydrochloric, 1 M	1.1 mL	23[c]	22.97
L27	56.2	Nitric, 1 M	3.7 mL	78[c]	79.66
L28	56.3	Nitric, 0.1 M	6.0 mL	78[c]	80.52
L29	56.3	Nitric, 0.1 M	4.8 mL	78[c]	82.80

a. Copper-coated steel BB shots (~4.5-mm diameter).
b. Pretreated copper-coated BB shots to remove copper coating.
c. Steel shots (~4.2 mm-diameter) with mercury inert coating.

- Early runs (Runs L1-L6) with copper-coated BB balls indicated that more interaction occurred with elemental mercury and BB balls than with elemental mercury and copper powder. The balls had a copper powder coating. When the copper coating was rubbed away, a silver (mercury) layer was exposed on the surface of the balls. The remaining experiments (Runs L7-L29) were performed using balls without a copper surface.
- Some of the runs resulted in the creation of amalgams resembling a silver putty that was soft and malleable. After a day, these "putties" became rock hard (Runs L7, L9, L10, L11, L15, L16, L21, L22, and L27).
- Instead of acid, 1 mL of water was used to determine if the copper only required a bit of moistening. The resultant amalgam was a darkened powder that had many tiny mercury balls throughout. It was reasoned that the water promoted the oxidation of the copper surface, whereas the acid helped dissolve and break away the oxide surface (Run L8).
- Some runs were performed on varying amounts of 1 M HNO_3 added. With no acid, there was nearly no amalgamation. With increasing acid volumes, the particle size of the amalgams increased (Runs L12-L19).
- The use of hydrochloric acid in the pretreatment produced a poorer amalgam (free mercury present) than was evident when nitric acid was used in the pretreatment (Runs L23-L26).
- Two of the runs, Runs L21 and L27 were performed with the actual contaminated mercury. These runs verified that the amalgamation procedure used in Run L16 would work for the actual waste to be processed.

Because of time constraints and the inadequacy of product requirements, the procedures adapted in Run L16 and verified for processing in Run L27 were to be used for the contaminated mercury. The resulting amalgams were required by the investigators to adhere to the following treatment residue criteria:

- Initial solid is a malleable mass
- Within 24 hours, the initial solid hardens into a nonmalleable solid
- No free mercury on visual inspection
- No free mercury upon centrifuge testing.

These treatment residue requirements were based on a target amalgam form of dental restorations. This form of amalgam can be shaped to occupy less space than other amalgam forms. With a rock-like structure, the elemental mercury will be well tied up and virtually immobile. The only question that remained was the ability of the amalgam to pass the TCLP for mercury (not a requirement for treatment). TCLP results will be discussed in the next subsection.

CASE STUDY: CONTAMINATED MERCURY AT THE INEL

The INEL currently has mixed waste in storage. One storage facility that handles mixed waste is the Mixed Waste Storage Facility, which is managed by the Waste Reduction Operations Complex (WROC) of EG&G Idaho. Treatment option studies were conducted on the bulk of material in storage, and specific treatments were assigned to the individual waste streams. The treatments that were selected for the waste were based on the following criteria: the type of hazardous contaminants present in the waste, the physical state of the waste, and the RCRA restrictions placed on treatments of certain contaminants and their physical state. The following list of treatments were to be used on the waste at WROC: incineration, solidification, ion exchange, macroencapsulation, amalgamation, and radioactive lead recovery. The particular waste that made this treatability study necessary consists almost entirely of radioactively contaminated elemental mercury. At the time of the treatability study, there existed one waste stream of contaminated mercury, amounting

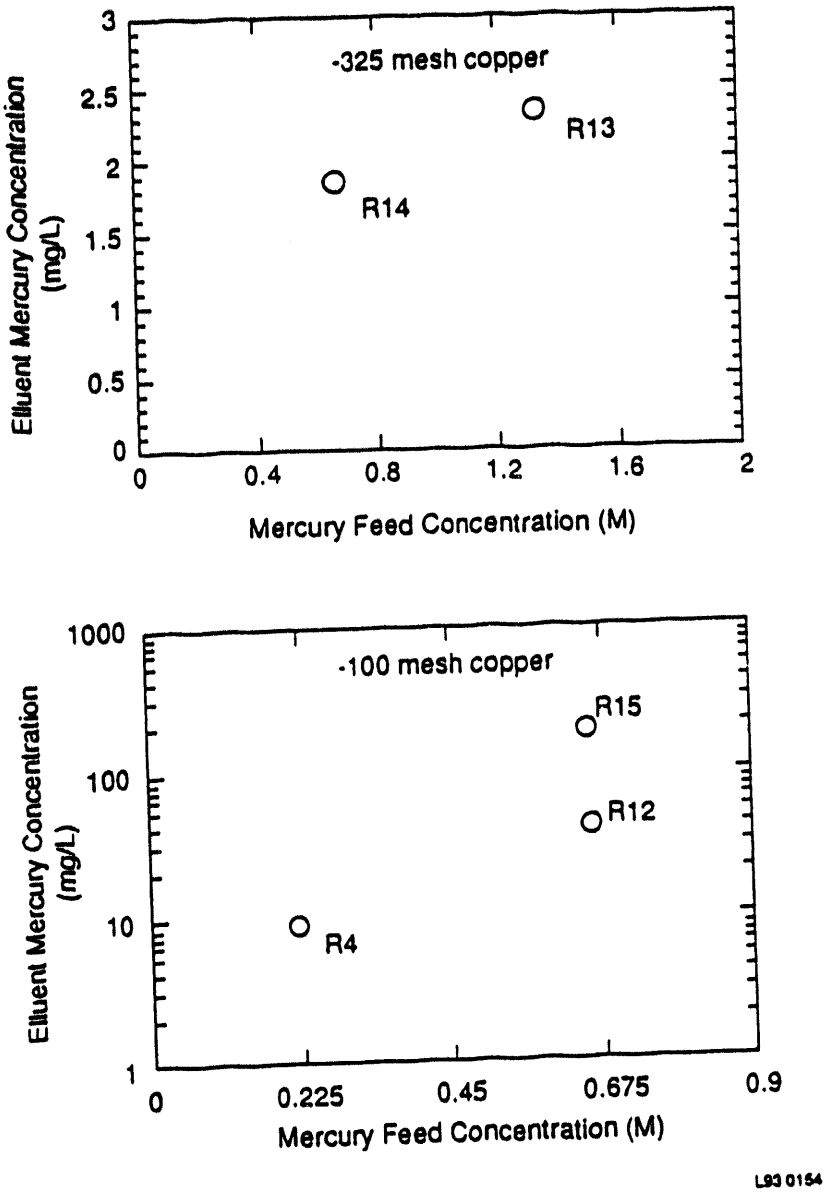

Figure 5. Effluent concentrations for filter bed runs.

to approximately 1.5 L. According to the generator's identification (Form EG&G-669), cobalt was present at a level of 3.5E-4 μCi/mL. The procedure developed from Run L16 and tested with contaminated mercury in Runs L21 and L27 was used for all of the radioactively contaminated elemental mercury. Table 4 describes this waste stream. The waste consisted of 1.5 L of mercury located in a drum referenced as barcode INEL540 at the MWSF. This waste had a low contact radiation value (0.1 mR), which allowed for normal retrieval of the mercury from this drum. The waste was contained in a bottle residing within the 5-gal drum. This bottle contained some water and debris associated with the elemental mercury. Because of the high density of the mercury, the debris and water floated on top of the mercury. The entire amount of debris and water was easily separated from the bulk of the mercury by simple decanting operations. (The debris and water still contained a small amount of mercury dispersed throughout, but would be treated in another study as a separate waste form having a different treatment standard.)

Table 4. Waste stream designated for amalgamation.

WERF code identification number	MWSF bar codes	Waste name	Radionuclide content
21-91	540	TAN metallic mercury	Co-60 5.25E-7 Ci (.35 nCi/mL)

In order to handle the 1.5 L of radioactively contaminated mercury, a systematic procedure was developed. The first task was to determine the number of scintillation vials, or any other type of small container, needed for mercury based on the total volume of mercury and an estimate of 7.5 mL per vial. Each of these vials was numbered and weighed with approximately 7.5 mL of mercury pipetted into each scintillation vial. This was done for all of the mercury and was performed in a spill pan in the hood using pipets. The weight of mercury was determined for each of these vials. All of the sealed vials of mercury were stored in a marked and designated area for radioactive materials. HDPE widemouth bottles (250 mL) were numbered to correspond to the numbered scintillation vials. After weighing each bottle, the formula, $W_{Cu} = 0.78 \times W_{Hg}$, was used to determine the appropriate amount of copper (-325 mesh) needed for each bottle. The numbers on the scintillation vials were matched with the widemouth bottles of copper, and all of these weights were recorded on a table. Seventy-eight steel balls (4-mm diameter) were placed into each bottle containing copper powder. The HDPE bottles were securely fastened onto wrist clamps attached to the wrist shaker (four bottles per shaker). All of the HDPE bottles were opened and 3.7 mL of 1 M HNO_3 was added to each of the bottles. The bottles were then closed and shaken on the wrist shaker at the highest speed for five minutes. The bottles were removed from the wrist shaker and opened in the hood. The appropriate numbered mercury vials were opened and the mercury contents were poured into the corresponding numbered amalgamation bottles. The caps were replaced tightly onto the HDPE bottles, and the bottles were reclamped and taped back onto the wrist shaker. The caps of the bottles were taped with yellow radiation tape to secure the caps during the shaking process. These bottles were shaken for 40 minutes at the highest setting of the wrist shaker. After shaking, the bottles were removed and returned to the hood and the amalgams were inspected for the presence of free mercury. A small sample (5 to 10 g) of amalgam was removed from every eighth bottle and stored in a sample container for centrifuge tests. The amalgams were placed into a disposable 1-L beaker, with a second lead-weighted 1-L beaker fitting over the top to assist in compressing and shaping the bulk of the amalgams. The amalgam samples obtained for centrifuge tests hardened within 24 hours and a centrifuge test was run on the hardened amalgam samples. The centrifuge machine (Fisher Scientific Centrific Centrifuge) was set to the highest speed and the amalgams were spun for 30 minutes. After the sample spinning was completed, the amalgam sample

was inspected to see if any free mercury had been separated away from the amalgam structure. The resulting amalgams were required by the investigators to adhere to the treatment residue criteria presented.

All of the processed radioactively contaminated mercury resulted in amalgams that met the requirements of the treatment residue criteria. The first batch consisted of sixteen 250 mL bottles processed on two wrist shakers. Although the resultant amalgams were acceptable based on the treatment residue requirement, characteristics of the amalgams based on earlier trials using the same procedure were dissimilar. One suspected cause was an inadvertent change in acid strength of stock solution. Batch C (Bottles 19–23) was performed using different acid molarities, and although the amalgams passed the treatment residue requirements, the characteristics were still different from the earlier runs. Batch B (Bottles 17–18) was to replicate the initial batch, but with only 2 bottles processed instead of 16. Using fewer bottles per batch, amalgams were produced having properties similar to the earlier trials. In comparing the results from Batches B and C, it was believed that the amount of time between steps resulting from the increased amount of bottles created an additional parameter with which to be considered. In subsequent batches, the number of bottles processed was reduced to eight (four per shaker). The total number of batches that were handled is shown in Table 5. A TCLP was performed on the treatment residues. Although the radioactively contaminated elemental mercury was successfully treated by amalgamation, the TCLP tests were needed to determine whether the treatment residues (amalgams) were hazardous due to the mercury characteristic. Four samples of amalgams were obtained and sent to TCT-St. Louis for testing. Two samples underwent TCLP analysis and two samples underwent corrosivity analysis. The results from the TCLP test showed that the two samples had mercury concentrations in the leach extract of 0.0391 and 0.0198 mg/L, respectively. These results have not yet been validated, but are currently undergoing the validation process. These numbers are well below the regulatory level of 0.2 mg/L, indicating that the amalgams are not hazardous. The amalgams are rendered as low-level waste that was targeted for disposal at a subtitle D disposal facility. At the INEL, the Radioactive Waste Management Complex is such a facility, and upon validation of the TCLP results, will be the chosen location for disposal.

RECOMMENDATIONS FOR SCALE-UP OF AMALGAMATION TREATMENT

For future treatment of radioactively contaminated elemental mercury, scale-up of the aforementioned process may be necessary. This would be especially true if more than 1.5 L of mercury were present. In order to treat all of the contaminated mercury in this treatability study, the treatment was performed in the laboratory under bench-scale conditions. Scale-up was not required because of the small quantity of mercury. Furthermore, scale-up would have potentially created vast amounts of hazardous waste from amalgamation trials. It was essential from a waste minimizational viewpoint to use less than 2 mL of noncontaminated mercury per trial run. If contaminated mercury waste existed in substantial amounts, it would not be efficient to measure out 7.5 mL of mercury per amalgamation bottle. Scale-up would require testing of equipment to determine if the process will proceed differently than what was observed during bench-scale runs. The bench-scale results would serve as a starting point for the scale-up procedure.

One type of apparatus that would serve as scale-up equipment for amalgamation is a paint shaker. This equipment can handle a fair amount of material and may adequately simulate the wrist shaker. A 5-gal paint shaker (Model 6 from Grenier and Co., Inc.) typically handles 60 to 80 lb, and has been tested to handle a maximum of 100 lb. The speed of mixing is reported to be 255 cycles/min. In bench-scale processing of contaminated mercury, there was approximately 7.5 mL of mercury for each 250-mL container. If this ratio is maintained, then about 570 mL of mercury (17 lb) would be processed in a 5-gal drum. Given the prescribed recipe for the contaminated mercury, the weight percentage of mercury in a charge is 50% when grinding balls are used, and 55% when no grinding balls are used. If a decision was made to process the maximum amount of amalgam in a given batch (100 lb), the amount of mercury processed would be 1.63 L (50 lb) using grinding balls or 1.84 L (55 lb) without grinding balls. Some initial tests will have to be run with noncontaminated mercury to see if there are any processing problems associated with scale-up. This could require up to 5 L of mercury to be purchased.

Table 5. Inventory of radioactive material treated by amalgamation.

Batch number	Bottle numbers	Batch number	Bottle numbers
A	1–16	11	104–111
B	17–18	12	112–119
C	19–23	13	120–127
1	24–31	14	128–135
2	32–39	15	136–143
3	40–47	16	144–151
4	48–55	17	152–159
5	56–63	18	160–167
6	64–71	19	168–175
7	72–79	20	176–183
8	80–87	21	184–191
9	88–95	22	192–197
10	96–103	23	198

If more bench-scale work is desired prior to full-scale activities, given proper funding support, further effects of certain key parameters can be investigated. These parameters include:

- Effect of grinding ball size
- Effect of the number of balls/mass of charge
- Effect of mass of charge/container size
- Effect of shaking angle
- Effect of higher shaking speeds.

The particular responses to the above effects would be the amount of free mercury in amalgams following centrifugation and mercury concentrations in solution following leaching of amalgams. If the free mercury levels are zero for several parameter conditions, a range of conditions for successful amalgamation would be determined. The procedure for leaching tests would not be required to be equivalent to the TCLP, since the results would merely represent process knowledge. Inherent to any leaching procedure set forth should be a way to prepare samples that have fairly uniform specific surface areas from one amalgam sample to another. This may require some size reduction, followed by sieving of the material.

CONCLUSIONS

- When amalgamation was performed with the mercury initially in solution, it was difficult to produce amalgams that would either exhibit no free mercury or would pass a centrifuge test.
- Copper was determined to be the better metal to amalgamate with mercury, based on test results in concert with equilibrium and kinetic considerations.

- Metal powders with small particle sizes will perform better in amalgamations due to increased surface area.
- A small addition of acid, in addition to grinding balls, are needed to achieve an acceptable amalgam form.
- The method of amalgamation used on the actual radioactively contaminated elemental mercury waste created an amalgam that was able to pass TCLP for mercury.

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PRELIMINARY DESIGN OF A BIOLOGICAL TREATMENT FACILITY FOR TRENCH WATER FROM A LOW-LEVEL RADIOACTIVE WASTE DISPOSAL AREA

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ABSTRACT. A New York State Energy and Research Development Authority (the Authority) funded treatability study identified biotreatment as the best technology to reduce the hazardous constituent concentrations below discharge criteria. Ion exchange resins were shown to reduce strontium-90 and cesium-137 concentrations of a low-level radioactive waste disposal trench leachate below release limits. Based on the results of this treatability study, the Authority has funded the design of a leachate treatment system. An activated sludge bioreactor and ion exchange resin columns will be components of the treatment train.

A discussion of the design and the design criteria for the treatment facility will be provided. Particular emphasis will be placed on the availability of off-the-shelf equipment and the modifications that will be required. Other issues which will be discussed are: tritium concentration concerns, secondary waste generation and processing, design codes, site layout and schedule.

INTRODUCTION

The New York State Energy Research and Development Authority (the Authority) owns and manages a State-Licensed Low-Level Radioactive Waste Disposal Area (SDA) at West Valley, New York. Water has migrated into the burial trenches at the SDA and collected there, becoming contaminated with radionuclides and organic compounds. In February 1992 the Authority signed an agreement with the Environmental Protection Agency (EPA) and New York State Department of Environmental Conservation (NYSDEC) which included an interim measure to install a system to remove, process and dispose of water from Trench 14. A treatability study of the contaminated trench water (leachate) was performed and determined the best available technology to treat the leachate and discharge the effluent. This paper describes the preliminary design of the treatment facility that incorporates the bases developed in the leachate treatability study.

HISTORY AND BACKGROUND

The SDA is located in the Authority maintained portions of the Western New York Nuclear Service Center (WNYNSC) which occupies 1354 hectares (3,345 acres) of land approximately 48 kms (30 miles) south of Buffalo, New York. The Authority holds title to the WNYNSC on behalf of the people of the State of New York. Under the West Valley Demonstration Project Act of 1980, the United States Department of Energy (DOE) has exclusive use and possession of approximately 81 hectares (200 acres) of the WNYNSC for the

performance of the West Valley Demonstration Project (WVDP) which is operated by the West Valley Nuclear Services Company (WVNS). The remainder of the WNYNSC is maintained by the Authority.

The SDA consists of two sets of parallel trenches occupying approximately 6 hectares (15 acres) of WNYNSC property (Fig 1). The SDA was constructed and operated by Nuclear Fuel Services Company, Inc. (NFS) as a commercial low-level radioactive waste (LLRW) disposal facility from 1963 to March 1975, when waste disposal operations were terminated. NFS monitored and maintained the SDA until March 1983, when management responsibility was transferred to the Authority.

During its operational life, the SDA received approximately 68,000 m^3 (2.4 million cubic feet) of LLRW initially containing approximately 26 PBq (700 KCi). The waste was received from various sources, including institutions, industries, governmental facilities, nuclear power plants, waste brokers, and decontamination facilities. The physical forms of the waste were extremely diverse. Most of the waste was disposed of in the original shipping containers, including 23-, 136-, and 250 L (5-, 30-, and 55-gallon) steel drums, wooden crates, cardboard boxes, cartons, fiber drums, and plastic bags.

Packaged waste was placed in long trenches excavated in the highly impermeable, silty till soil native to the site, and covered with 1.2 to 2.4 m of excavated soil. Due to the character of the soil and the wet climate, water management problems were experienced from the very early years of operation. Despite efforts to address the problem, water accumulated in open, uncompleted trenches, as well as in covered, completed trenches. Trench 14 has historically exhibited the most significant increases in water levels.

Water has collected in trench 14 due to the lateral migration of ground water and the percolation of precipitation through the trench cap. As the water contacts and percolates through the disposed trench wastes, it becomes contaminated with radionuclides and organic compounds. The resulting leachate, with its radiological and hazardous constituents will be the subject of the treatment system described in this report.

EXISTING FACILITIES

The Authority has installed emergency pumping and storage capabilities for storing trench leachate immediately adjacent to Trench 14 between the trench and the access road (west side). The storage capacity consists of the 41,800 L (9200 gallon) collection tank and two 95,500 L (21,000 gallon) stainless steel tanks.

The collection tank is housed in a weatherproof, heated building with the lower portion built of concrete to provide a secondary containment enclosure. In addition to the tank, a pumping system has been installed to pump leachate from the trench to the 41,800 L (9200 gallon) collection tank.

A ventilation system has been provided with the pump skid to ensure safe venting of the tank during fill operations. The ventilation system consists of a charcoal filter to remove organic pollutants and a HEPA filter to remove particulate matter. A tritium monitoring system measures the amount released during operation of the pump skid, as well as during normal tank venting operation.

The two storage tanks are installed in a steel framed synthetic berm. A non-heated, weatherproof building protects these tanks from the environment. Both tanks have immersion heaters installed for freeze protection. Each tank is connected to the pump skid and ventilation system in the collection tank building. Local high level and remote high-high level alarms are designed into the system.

TREATABILITY STUDY RESULTS

The preliminary design presented in this paper is based on literature review, accepted engineering practices, and the treatability studies conducted by Ecology and Environment, Inc. (E&E) in 1990 and 1991-1992. The initial treatability study (1), was limited to the treatment technologies of carbon adsorption and ion exchange. The initial study, conducted in a trailer-based field laboratory at the SDA, showed that while carbon was effective in removing target indicator volatile organic compounds (VOCs), it was not effective in reducing the five-day biochemical oxygen demand (BOD_5) without consequent generation of unacceptably large quantities of spent carbon residue. Ion exchange was found to be effective in reducing cesium-137 concentrations.

Based on the results of the initial treatability study, the Authority elected to perform more extensive bench-scale treatability studies to examine a greater range of treatment technologies specifically, biological treatment, UV oxidation, and evaporation/distillation, as well as additional studies of carbon adsorption and ion exchange. One of the goals of the additional treatability studies was to identify and develop treatment technologies that, unlike direct carbon treatment, minimized the amount of waste generated. Waste minimization is an important goal, considering that all wastes generated by this process will likely be regarded as mixed wastes, for which disposal options are limited. Thus, technologies that destroy the hazardous component of the waste such as biological treatment and UV oxidation - were pursued. The goal of waste minimization has been further pursued throughout the preliminary design of the selected treatment process.

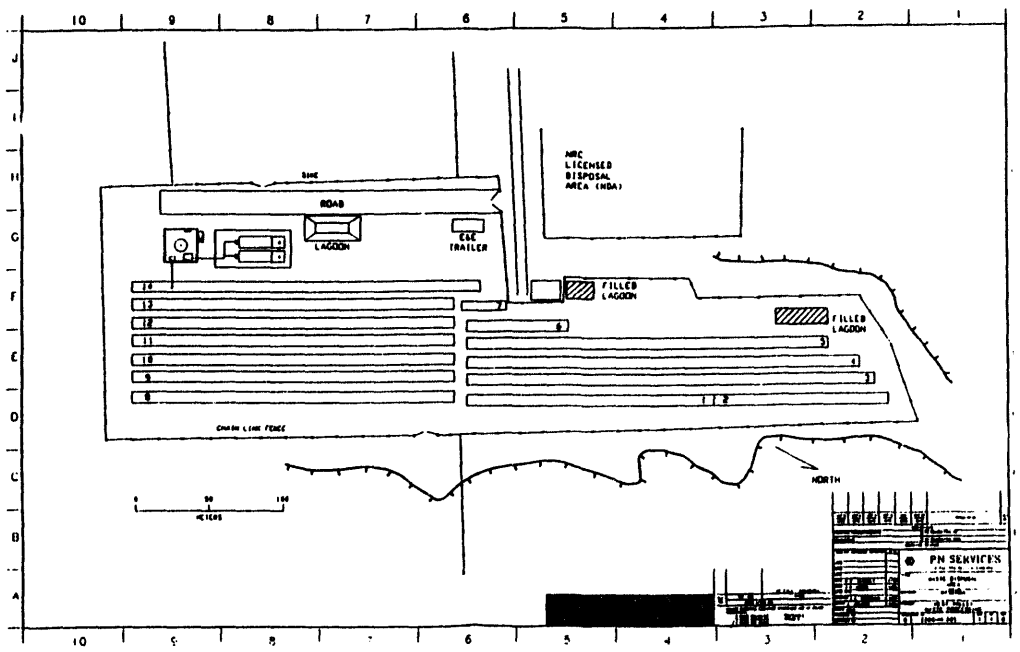

Figure 1.

The second treatability study (2) demonstrated that biological treatment, followed by filtration, carbon polishing, and ion exchange is capable of treating the trench 14 leachate.

The preliminary design is also based on the flow rate constraints resulting from the presence of tritium in the effluent. Due to the dilution required for discharge, an estimated 73,200 - 159,000 L (16,100 to 35,000 gallons) of treated leachate can be discharged per year. To handle this range of annual leachate volumes, the daily batch treatment size basis has been set at 4,550 L (1,000 gallons).

The system has also been designed to be flexible. Batch system biotreatment, rather than continuous treatment provides flexibility in operational schedule, mainly by varying the aeration duration. Lower throughputs can be achieved by increasing aeration duration to two days or more. Higher throughputs can be achieved by either increasing the amount of leachate charged to the bioreactor (this is allowed due to bioreactor oversizing) or, if operational experience allows, by decreasing the aeration time. Operational flexibility is also enhanced by the fixed-bed processes of the downstream physical treatment train. The rate of flow through the fixed beds can be changed, up to a point, without affecting their performance. The treatment train is sized to handle up to two times the design basis throughput of 4550 L/day (1,000 gallons).

PRELIMINARY DESIGN OF TREATMENT SYSTEM

General Process Description

Using the existing system, leachate is pumped from the sump in Trench 14 through a filter and then to the 42,000 L (9,200 gallon) collection tank. The leachate is pumped to the bioreactor tank in the adjacent biotreatment facility. The bioreactor system receives the leachate in a 27,200 L (6,000 gallon) bioreactor tank where the liquid is batch-processed to remove organic contaminants. The process uses mixing and aeration which enhances the development of a microbial biomass to biologically destroy organics. This mixing process is followed by a settling time. The entire process can be completed in a one day time frame.

The bioreactor supernatant is pumped to a 27,200 L (6,000 gallon) holding tank in the physical treatment system. This tank operates as an interface surge tank that links the biotreatment system with the continuous physical treatment system. Continuous operation of the carbon and zeolite beds of this system maximizes the life of these media and minimizes the amount of waste by-products produced. Particulates in the supernatant process stream are then treated through activated carbon columns. The final treatment pass is through zeolite ion exchange units where radionuclides (^{90}Sr & ^{137}Cs) are removed. The clean water is pumped to storage tanks for subsequent discharge to the permitted outfall.

Gases and vapors produced during system processes are exhausted through an air dryer, HEPA filter, and activated carbon chamber within the off-gas system. This discharge is continuously monitored to detect any potential breakthrough.

The sludge produced in the bioreactor is pumped to a 9,100 L (2,000 gallon) aerobic digestion and holding tank in the waste sludge system from where it is subsequently dewatered and packaged. The packaged waste is stored within the facility for further disposition.

Process control of the system will be provided by a combination of online monitors and analysis of grab samples. Online monitoring will be limited to pH and dissolved oxygen measurement of the bioreactor and the aerobic digester/sludge holding tank. The analysis of process samples will be conducted in an onsite laboratory and, to a lesser extent, outside analytical laboratories.

For the preliminary design, including provisional laboratory requirement, the analyses to be conducted onsite

have been selected. The parameters to be analyzed onsite are:

- 5-day biochemical oxygen demand;
- VOCs by gas chromatography;
- Total and volatile suspended solids;
- Total phenols;
- Total organic carbon.

In addition, the laboratory will be designed to allow the execution of limited bench scale tests should they be necessary during the pilot phase of operation. The only potential tests which may be considered at this time include column testing of ion exchange to identify ways to further minimize the zeolite consumption rate, sludge flocculation and settling tests, and possibly limited biomass development activities. The need for these tests will be evaluated and defined during the planning of pilot phase activities during the final design stages.

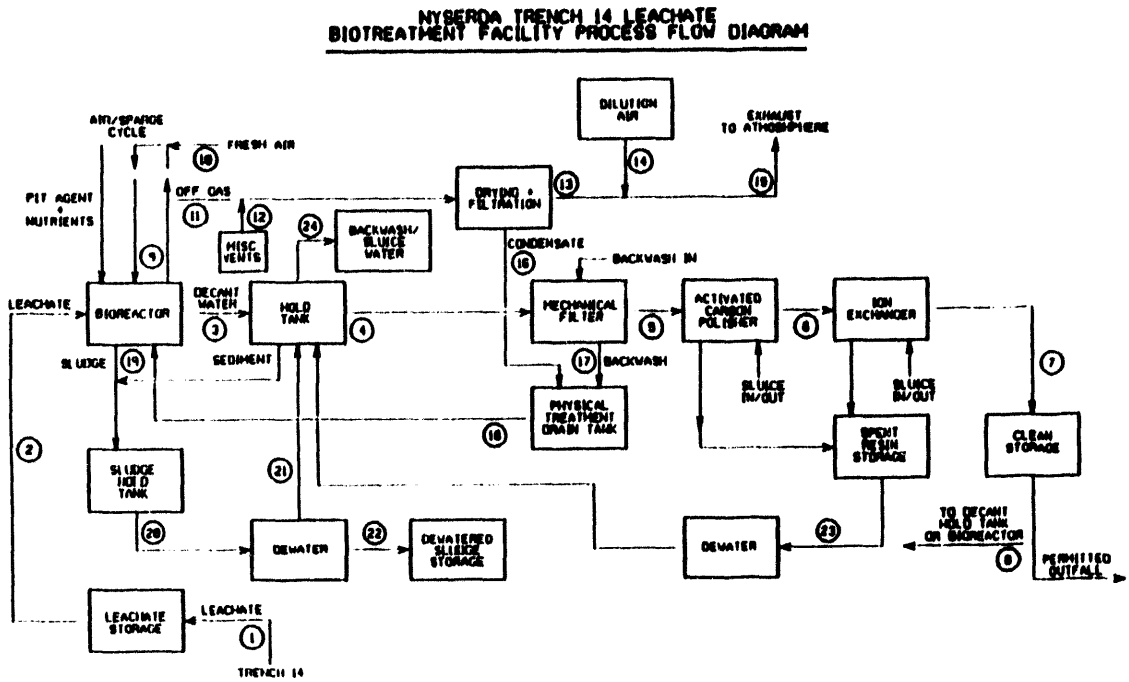

Figure 2. NYSERDA Trench 14 leachate
Biotreatment Facility Process Flow Diagram

Bioreactor Phase

The bioreactor will be a completely enclosed aerobic batch suspended-growth system. The bioreactor is a 27,200 L (6,000 gallon) vessel equipped with ports for acid, base, nutrient, polymer or other chemicals, and leachate addition (Fig 3). The bioreactor will receive leachate from the 42,000 L (9,200 gallon) leachate storage tank through the leachate transfer pump. The leachate storage tank will normally be kept full

utilizing the existing Trench 14 sump pump. This action will keep the leachate temperature essentially constant at the leachate storage building temperature. Process flow to the bioreactor will go through a flow totalizer which monitors the leachate volume transferred from the leachate storage tank. Since a portion of the leachate transfer piping will be located outdoors, process line heat tracing and spill/pipe break containment will be provided. Acid or base addition will be performed on a batch-specific basis if the pH exceeds the preferred range of 6 to 9. The dissolved oxygen level will be monitored and used to set the bleed rate. If high levels of dissolved oxygen (i.e., greater than 6 mg/L) are recorded, the bleed and make-up air flow rates will be reduced. Bioreactor exhaust air will be recycled to minimize the amount of tritiated-water-laden gas sent to the off-gas treatment system. After sixteen to twenty hours of aeration, agitation will stop and the mixed liquid allowed to settle. After settling, supernatant will be decanted through multiple ports located at varying elevations or through a floating decanter mechanism.

Sludge settled at the end of each batch run will be retained in the bioreactor for the next batch. When sludge levels increase to necessitate sludge wasting, sludge will be transferred to an aerobic digester/holding tank. Based on the Engineering Report (3) results, it is estimated that 3,400 L (750 gallons) of sludge will be produced per 22,750 L (5,000 gallons) of leachate processed. This tank will aerobically digest the biological solids to minimize the amount of sludge to be further processed. The tank would also act as a biomass source for re-inoculation of the bioreactor in case of loss of viability of the bioreactor biomass.

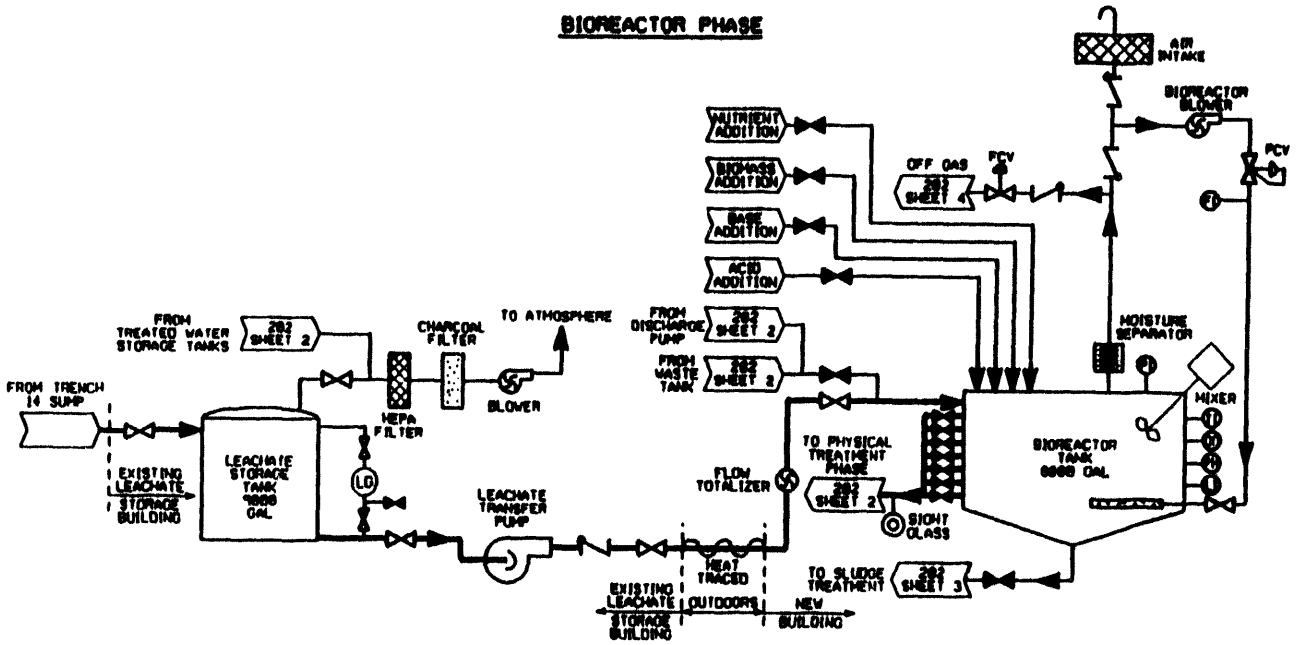

Figure 3. Bioreactor Phase.

Physical Treatment Phase

The primary source of fluid in the physical treatment process is from the bioreactor (see Figure 4). At the completion of each bioreactor batch cycle, the tank suction is provided via a multi-point decant manifold. Tank discharge is supplied to the decant hold tank. Supernatant is withdrawn from successively lower decant ports (or, depending on the bioreactor selected, a floating decanter) until the sludge level is reached. The point at which sludge has been reached will be determined visually through a sight glass in the decant line.

The physical treatment feed pump provides sufficient head to process the water from the decant hold tank through the treatment train to the treated water storage tanks. A manual flow control valve is used to establish flow as required for the configuration in use. The physical treatment train is a three stage arrangement, normally aligned for series flow. Each vessel is fitted with drain, test/flush, isolation and bypass valves.

The first physical treatment stage consists of two back-washable filter vessels capable of providing mechanical filtration to remove suspended solids. Valves for the filters are capable of remote operation and will provide automatic backwash capability when high differential pressure across the filter(s) is encountered. The backwash line is routed to the physical treatment drains tank. This tank also is utilized to drain the treatment system vessels (filter, carbon beds and ion exchangers) when required for maintenance. The contents of the drains tank can be transferred to the bioreactor by manual operation of the drains transfer pump.

Downstream of the filters are two activated carbon polishing beds which remove any remaining organic contaminants. These units provide the treatment system with the capability to compensate for bioreactor upsets and the availability to remove non-biodegradable contaminants regulated under State Pollutant Discharge Elimination System (SPDES) permit should they be present in the bioreactor effluent. The carbon beds will remove organics that are normally destroyed in the bioreactor to less than the discharge permit concentrations, if for some reason (i.e., process upset) the organics escape destruction in the bioreactor. Based on the Treatability Study results it is expected that a minimal amount of carbon will be utilized to treat the leachate and therefore the vessel size was determined based on required residence time for the particular process flow rate. The carbon beds will be operated in a series flow configuration with the first vessel as the primary polisher and the second acting as a backup in case of breakthrough.

When carbon bed breakthrough occurs, the valves will be realigned to establish flow to the backup vessel. This vessel will now act as the primary bed. The carbon in the original primary polisher will be sluiced out and replaced with fresh carbon. This column would then be returned to service, acting as the backup column. This arrangement will allow operation and maintenance flexibility during upset conditions.
The final stage of the treatment train consists of two ion exchange columns which contain zeolite medias. These units are designed to remove the radionuclides ^{90}Sr and ^{137}Cs. The ion exchange unit valves will be capable of remote operation. Remote valve operation will be utilized during sluicing operations and when vessels need to be switched in and out of service. The ion exchange vessels will be operated in series. When breakthrough of the first vessel occurs, the second vessel will be aligned to remove the radionuclides. The spent vessel contents will be sluiced out, refilled with fresh zeolites, and returned to service as the second vessel. Based on the Engineering Report results, it has been estimated that
500 kg (1100 lbs) of zeolites will be used to treat 91,000 L (20,000 gallons) of leachate.

Both the carbon and ion exchange columns are designed for sluicing the media to the spent media tanks. The sluicing operation is conducted using the backwash/sluice pump with fully treated water as the process fluid. The spent media storage tanks are sized to accommodate multiple vessel sluicings. The storage tanks are commercially available radwaste liners typically used in the nuclear power industry for storage, dewatering and transportation of ion exchange medias. After the contents of the ion exchange vessels and

carbon beds are sluiced to the spent media tanks, the tank will be dewatered utilizing a vacuum dewatering pump then discharged to the decant hold tank.

The treated water flows through a flow measuring device into the two 91,000 L (20,000 gallon) treated water storage tanks. A discharge pump will process the treated effluent to an approved outfall. The piping will also be designed with a discharge path local to the treated water storage tanks, in case transport by tank truck is required.

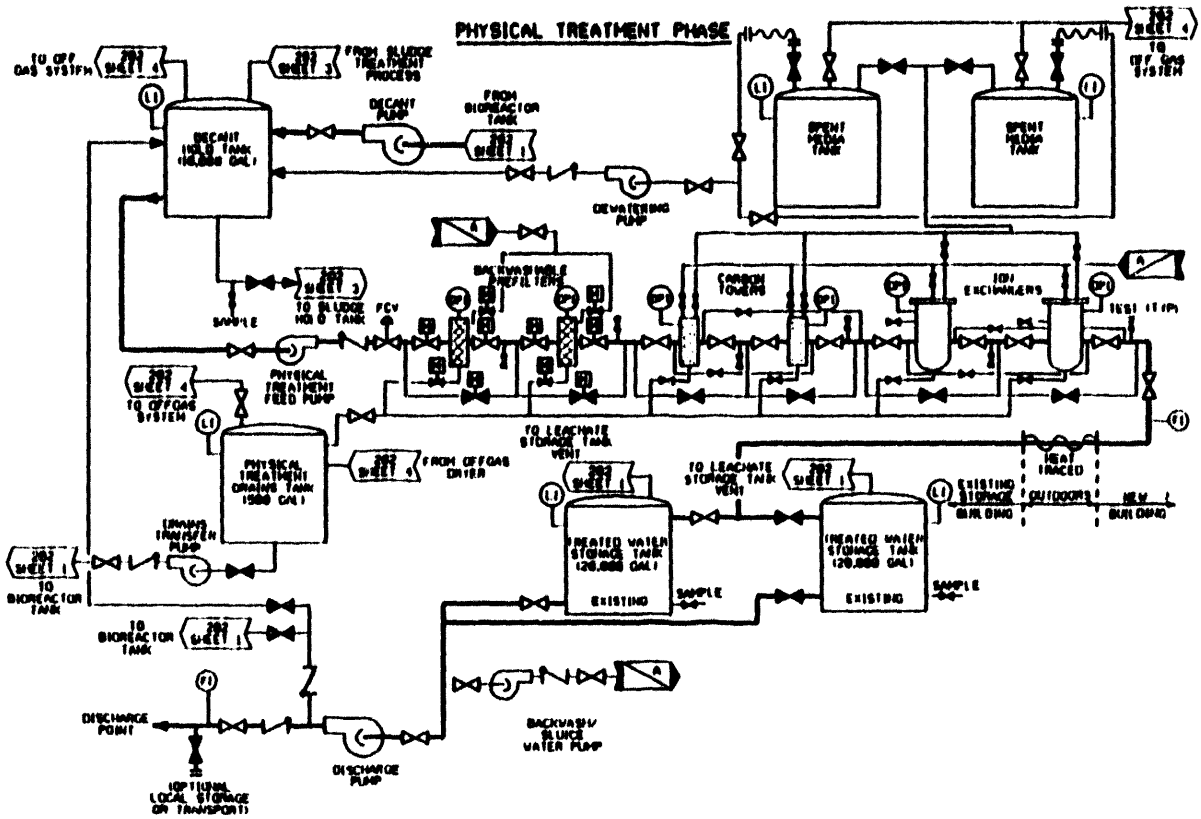

Figure 4. Physical Treatment Phase.

Off-Gas Treatment Phase

During operation up to 0.024 m^3/s (51 cfm) of bioreactor sparging air will be exhausted through the offgas system (Fig 5). The system is designed to handle up to .028 m^3/s (60 cfm) offgas to account for possible increased treatment rates and vapors from process vents. This sparging air will be drawn through a flow control valve downstream of the bioreactor vent moisture separator where it will be mixed with air vented from various contaminated tanks. The volume of bioreactor offgas will decrease over the course of the daily biotreatment cycle, as less substrate remains for consumption.

The offgas will pass through an air treatment train consisting of a dryer, HEPA filter and activated carbon chamber. The dryer will be a refrigerant industrial gas dryer. This unit will condense half the vapor contained in the offgas, reduce the tritium content and return the condensate to the physical treatment system for further processing. The dry offgas will be directed into HEPA filter. Particulate carryover from the offgas will be removed. This particulate will remain in the filter until periodic filter replacement. The offgas will then proceed through the activated carbon chamber where volatile organics will be removed. The activated carbon beds will also require periodic replacement. Based on the Engineering Report results, it has been estimated that 15 kgs (33 lbs) of carbon will be consumed per 91,000 L (20,000 gallons) of treated leachate.

At this point, the offgas will be drawn through the offgas fan and mixed with dilution air to further reduce the radioactive concentration of the remaining uncondensed tritiated water vapor.

An air sampling port, located downstream of the dilution air supply and inside the treatment structure, will allow analysis of the offgas to monitor releases and provide indication of offgas filtration breakthrough.

Waste Sludge System

Aeration and mixing are stopped for a period of time during the final phase of the bioreactor cycle to allow the solids to settle to the bottom of the bioreactor vessel as sludge. Since the bioreactor is designed to operate with up to 9,100 L (2,000 gallons) of accumulated sludge, this settling action will occur for several cycles before the sludge is moved to the sludge hold tank. See Fig 6 for the waste sludge process diagrams.

The 9,100 L (2,000 gallon) sludge hold tank will hold 4,550 L (1,000 gallons) of sludge from the bioreactor. The sludge in the hold tank is aerated to keep the biomass viable and digested to minimize the amount of solids requiring ultimate storage/disposal. The bleed air from the sludge hold tank is routed to the bioreactor offgas system for subsequent filtration, dilution and release.

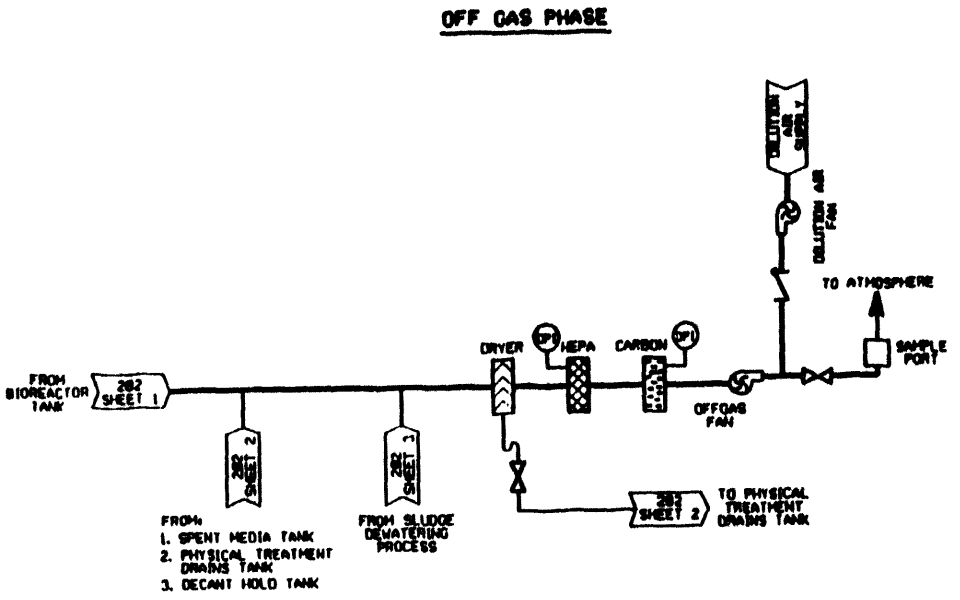

Figure 5. Off Gas Phase.

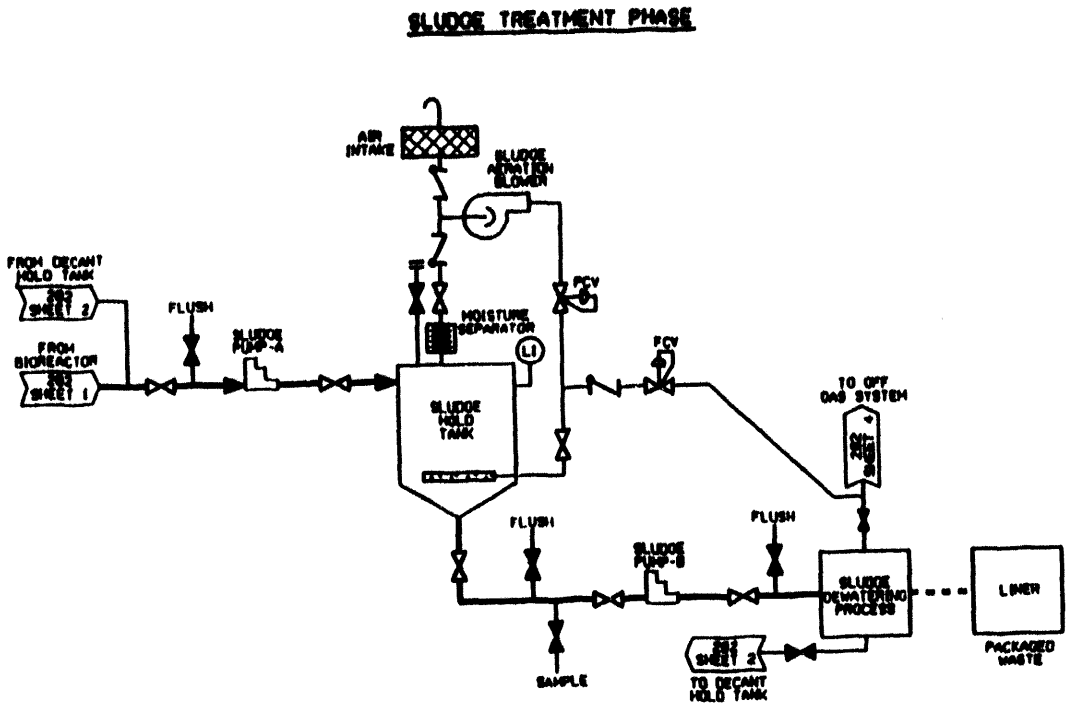

Figure 6. Sludge Treatment Phase.

The next step in the process is drying the sludge in a volume reduction system utilizing an evaporator to dry the waste stream to a powder form.

The sludge will be introduced to the dryer through a waste supply valve. When the liquid level in the dryer reaches a predetermined level, (high level) a differential pressure switch will automatically shut the waste valve. The sludge is then heated and steam vapor is pulled from the dryer through the condenser heat exchanger. This condenser is cooled by a chilled water system. The condensate is routed to the condensate reservoir from which it can be returned to the decant hold tank. After approximately three hours the dryer will boil down to the low level. At this time, the waste supply valve will be opened and additional waste will enter the system, bringing the concentration back up to the high level. Three transfers will be performed for each batch cycle.

The dry out phase begins with the end of the third transfer - the dryness of the material is verified by monitoring several system parameters, as well as a visual observation through the site glass.

Upon verification of dryness, the agitator helix moves the material to the pneumatically operated discharge valve located at the bottom center of the dryer shell. The material is discharged into the burial container using gravity.

The packaging enclosure, which houses the burial container, is kept under a negative pressure and vented through a HEPA system. This allows the operator to open the enclosure door to cap and remove the burial container without releasing contaminated particulate. This subsystem will work as a totally contained unit.

GENERAL ARRANGEMENT

The major design considerations implemented in the facility layout are personnel radiation exposure/equipment contamination (ALARA) design features, process flow logistics, flexibility for future operation at increased process flows, and adequate space for operations and maintenance of equipment.

The general arrangement of the biotreatment equipment is shown in Fig 7. The majority of the biotreatment system equipment will be housed in the new 174 m^2 (1875 ft^2) facility. This building will be located south of the existing leachate storage building. The building will be constructed of a steel frame with insulated sheet metal siding and built on a reinforced concrete slab. The exterior walls which enclose the spent media tanks and ion exchange units will be made of reinforced concrete to provide radiation shielding.

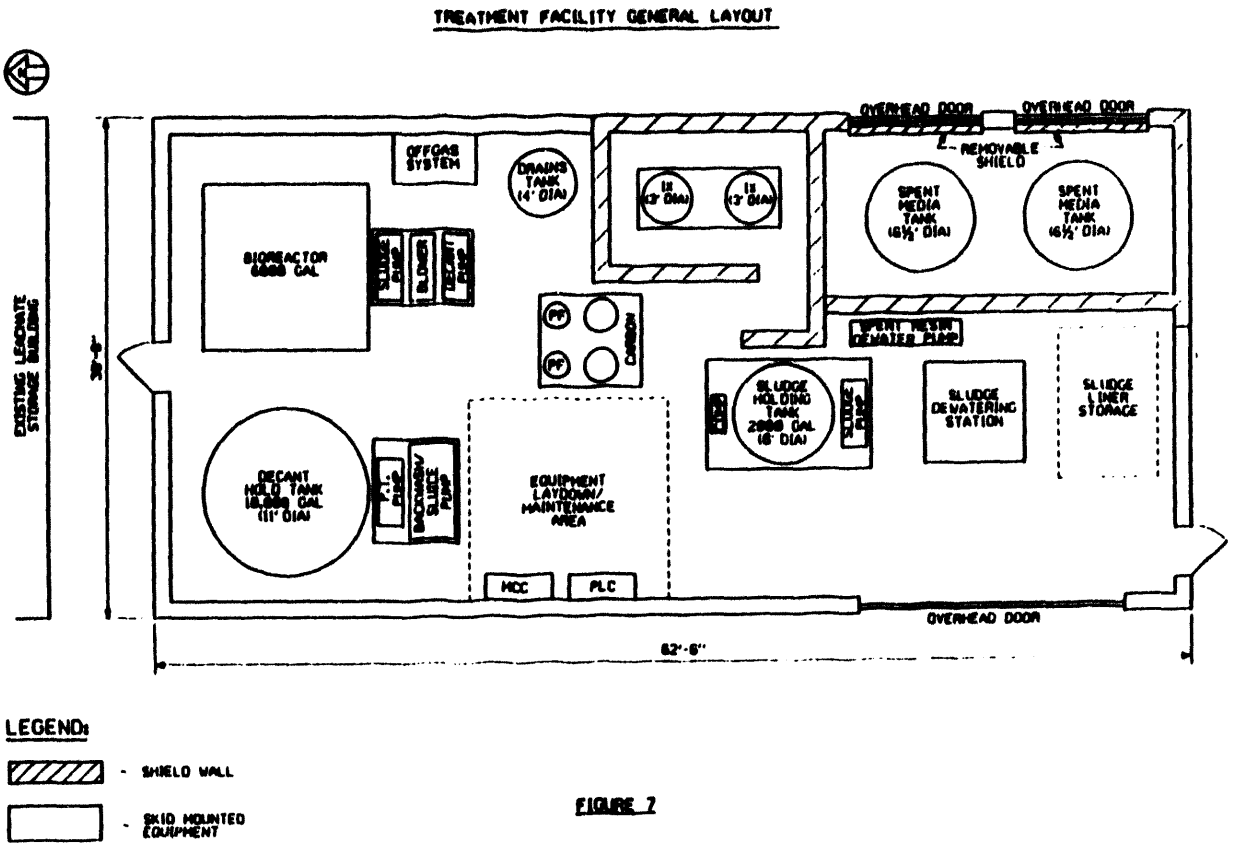

Figure 7. Treatment Facility General Layout.

The equipment layout has been arranged to provide a waste processing flow path from the north side to the south side of the building. The bioreactor will be located in the northeast corner of the building. The auxiliary equipment required to support the bioreactor operation will be located adjacent to the bioreactor tank. This arrangement will minimize piping around the bioreactor and simplify system operation, equipment monitoring, and maintenance.

The decant hold tank will be adjacent to the bioreactor tank to minimize process piping between equipment.

The decant hold tank will be located in the northwest corner of the building where it will have the least impact on floor space.

The filters and carbon beds are skid mounted and will be situated to optimize the space necessary for ease of operation and maintenance. The drains tank will receive filter backwash and will be in close proximity to the filters to minimize pipe routing. The ion exchange units are located in a separate cubicle in an effort to shield radiation and reduce exposure to personnel in the building.

The southern section of the building is arranged to house the sludge holding and dewatering/ treatment equipment. A separate cubicle will be set-up to shield the spent media tanks. Large overhead doors have been incorporated into the design and will be located in the southeast and southwest walls. These doorways will be sized to facilitate handling/removal of the spent media tanks and the sludge storage containers.

Adequate space has been provided in the floor plan for equipment laydown and maintenance. Aisle space has been provided along the west wall to facilitate equipment/spent media handling with a forklift.

The building design will also include a curbing feature which will have the capacity to contain a spill of the full contents of the largest tank in the building should catastrophic failure occur. An additional 0.15m (6 in) free board is included in the curbing design.

The building is usually uninhabited and as such will be maintained at 15.5°C/32.2°C (60°F/90°F) during winter and summer conditions. Although temperatures may vary, they will not pose an adverse effect on the treatment system process. Auxiliary heaters will be installed to provide heat during winter conditions.

CONCLUSION

The preliminary design of a mixed waste treatment system at the SDA has successfully incorporated the technologies identified in the bench-scale Treatability Study. This design provides the flexibility necessary to fully process the specified range of influent leachate flows while minimizing the resultant waste volumes. The resultant effluent water stream will meet the SPDES discharge criteria for all compounds except tritium (which will be diluted at the site outfall).

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EVALUATION OF TREATMENT TECHNOLOGIES FOR MIXED WASTE SOIL CONTAINING MERCURY

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ABSTRACT. Treatment processes are being evaluated for conversion of mixed waste soil (containing mainly ^{137}Cs, ^{90}Sr, mercury, organics, etc.) to a radioactive waste. A preliminary evaluation was conducted on soils spiked with mercury and trichloroethane using vacuum retorting and stabilization methods. The results of these experiments verify good removal and fixing of mercury. A commercial thermal desorption process was next tested on a representative mixed waste soil sample. The thermal process uses an externally-fired rotary dryer, and in these tests, the dryer was operated at both 370 and 480 C with a residence time of 85 minutes. The volatiles are driven off the soil by heat, then transported by nitrogen carrier gas. The carrier gas flows to a gas treatment system where organic, mercury and water vapors are removed and recovered from the gas. The thermal process effectively removed organics and mercury from the mixed waste soil sample.

INTRODUCTION

Energy Technology Engineering Center (ETEC) is closing a surface impoundment located on a three acre portion of Rocketdyne's Santa Susana Field Laboratory (SSFL), identified as the former Sodium Disposal Facility (SDF). The SDF is essentially an open soil field area with local regions of contamination. During the remediation of the former SDF, it is anticipated that approximately 300 tons of low level radioactive soil, mixed with hazardous materials, (mercury, organics, etc.), will be generated. Treatment processes are being evaluated for rendering the mixed wastes as low specific activity wastes acceptable to the Hanford, Washington disposal site. The mixed waste soil will be shipped to an EPA permitted facility at SSFL for interim storage, then treatment.

DESCRIPTION OF TREATMENT PROCESSES

Retorting and stabilization experiments were performed on spiked-clean soil samples taken outside the former SDF. The retorting experiment (Fig. 1) was operated at approximately 370 and 480°C under vacuum (3-5 Torr) with periodic mixing. The samples of soil spiked with mercury and trichloroethane were also stabilized with activated carbon and sulfur by mixing various amounts of the reagents with soil for 8 hours.

Mixed soils from the SDF were treated using a small pilot-scale thermal desorption process at Clemson Technical Center's mixed-waste treatability laboratory(1). The laboratory scale patented X*TRAX TM process used an externally-fired rotary dryer, and in these tests, the dryer operated at both 370 and 480°C with a residence time of 85 minutes (Fig. 2). The volatiles were transported from the soil by nitrogen gas.

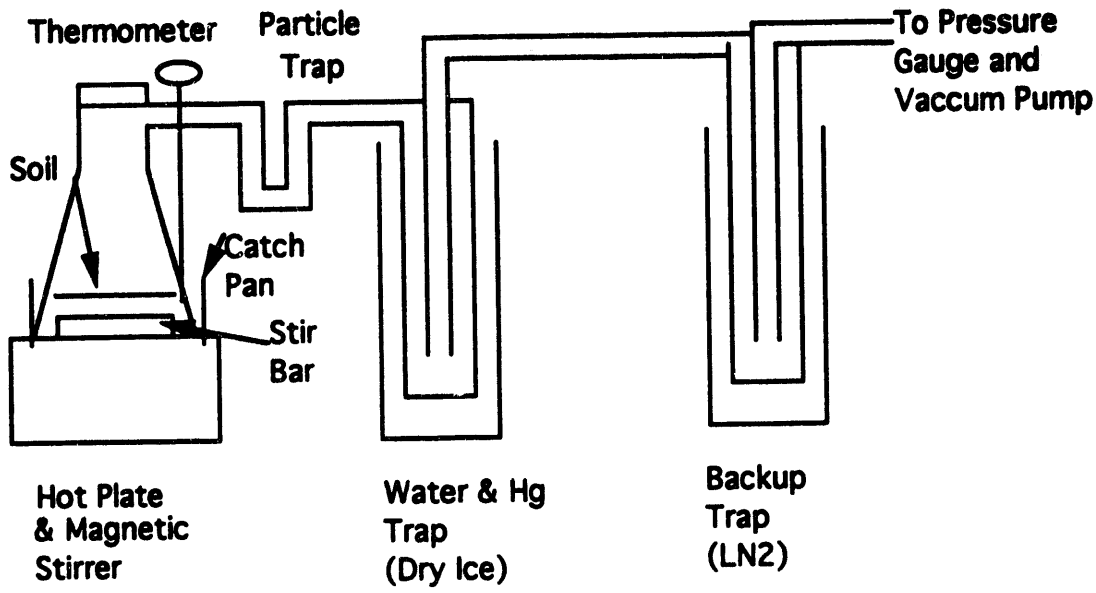

Figure 1. Laboratory Retorting Apparatus.

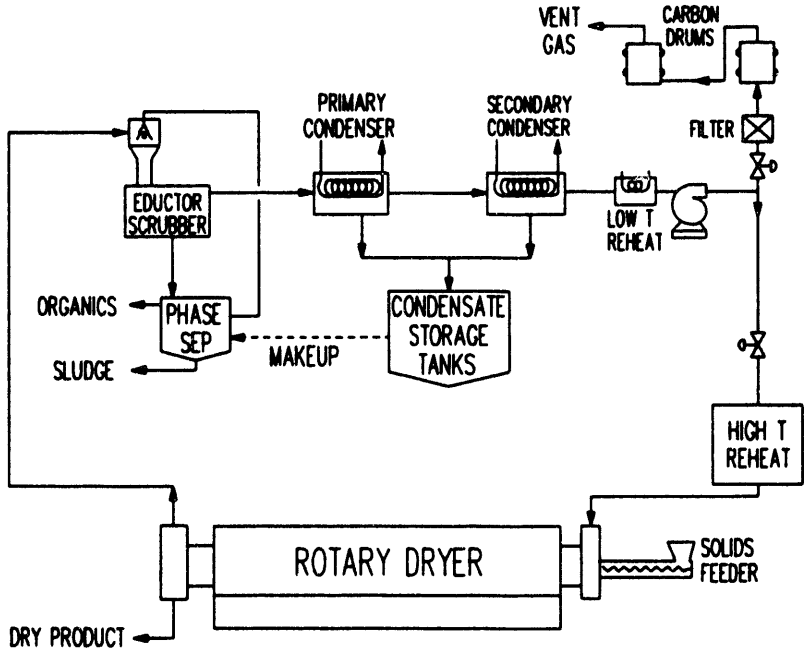

Figure 2. X*TRAX Process Flow Diagram.

The carrier gas flowed to a gas treatment system where organic, mercury and water vapors were removed and recovered from the gas. The gas was recycled in the process. Stabilization experiments consisted of mixing the soils with portland cement, pozzolanic materials, activated carbon and sulfur.

RESULTS OF TREATMENT

Results of separate retorting and stabilization experiments performed on mercury and trichloroethane spiked soil are shown in Table 1. The 4-hour retorting experiment appeared to yield excellent mercury removal. Samples of soil stabilized with activated carbon and sulfur also passed TCLP(2). The results of these experiments verified good removal (by retorting) and (by stabilization) fixing of mercury and trichloroethane.

Table 1. Spiked soil retorting and stabilization experiments.

Soil:	Original	Retorted	Stabilized*
Total Hg (mg/kg):	10,800	290	4700
TCLP Hg (mg/L):	N.D.**	0.052	0.009
Total TCA (mg/kg):	10,400	N.D.	N.D.
TCLP TCA (mg/L):	N.D.	2.1	95.0

Spiked soil stabilization experiments using individual reagents:

	Total Hg (mg/kg)	TCLP Hg (mg/L)
Starting Soil	3200	0.039
1% GAC***	2600	0.014
1% Magnetite	670	0.032
0.4% Sulfur	920	0.039
2% Sulfur	120	0.018

* Using mixture of all three reagents.
** Not determined.
*** Granular Activated Carbon.

The results of the X*TRAX treatment of actual mixed soil from the SDF are shown in Table 2. The mercury and oil/grease concentrations in the feed were significantly reduced by the X*TRAX process. Mercury concentration of the treated soil was determined to be less than 4 mg/kg. This represents a removal efficiency of nearly 99.9% at the 480°C steady-state operating condition. Oil/grease concentrations were reduced from 4,770 mg/kg to less than 40 mg/kg at the 480°C operation condition. This represents a removal efficiency of 99%. Neither the untreated nor the treated waste exhibited TCLP characteristics for mercury, chromium or trichloroethylene.

A good separation was achieved between the radioactive components of the waste (as measured by gross alpha/beta activity) and the hazardous components (mercury). The treated soil contained the bulk of the radioactivity with some carryover transferred into the wet-scrubber sludge. The wet-scrubber sludge is dewatered and recycled back through the pilot and full-scale X*TRAX systems. What little residue that remains can be blended with treated product to render the final product as a non-mixed waste. The mercury removed from the original soil sample was apparently deposited in the condensers and connecting piping. The gross alpha/beta activity of the condenser water was less than the EPA's maximum containment level (MCL).

Table 2. Treatability results for selected constituents.

900 °F Steady State Run			
Constituent	Feed Concentration (mg/kg)	Product Concentration (mg/kg)	Percent Removal
Mercury	2770	3.12	99.89
Oil/Grease	4770	39,8	99.17
TCLP Mercury	0.138	N.D.	
TCLP Chromium	N.D.	N.D.	
TCLPTCE	N.D.	N.D.	

N.D. = Not detected.

Because TCLP (chromium and trichloroethylene) were below detectable levels in the untreated soils, only mercury was of concern. Measurable amounts of TCLP mercury, 0.138 mg/L, were present only in the untreated soil sample (prior to treatment by X*TRAX). TCLP mercury levels were reduced to 0.005 mg/L in this soil by stabilization with portland cement/sulfur/water. The portland cement produces alkaline conditions that enhance the formation of sulfide ions from sulfur. The sulfide ions react with mercury to form insoluble mercuric sulfide. Treatment of the SSFL soil with portland cement/water only resulted in TCLP mercury levels of 0.068 mg/L. This was not a true reduction in leachability but was due to the dilution caused by adding cement and water to the soil. Treatment of the SSFL soil with sulfur only or a sulfur/water mixture increased TCLP mercury levels to 1.2 - 3.3 mg/L. The reason for this increase is unknown.

CONCLUSIONS

The X*TRAX system was successfully applied to the SSFL soils. Excellent mercury and oil/grease removals were achieved. The treated exhibits the disposal site criteria for mercury and hydrocarbons. Virtually all of the radioactivity was confined to the treated soil and wet-scrubber sludge (which is recycled on the pilot and full-scale systems). The gross alpha/beta activity of the condensate collected was less than the drinking water regulatory limit. The X*TRAX process will be applied to approximately 300 tons of low level radioactive soils from the SDF containing mercury and oil/grease contamination.

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TREATABILITY STUDY OF AQUEOUS, LAND DISPOSAL RESTRICTED MIXED WASTE CONTAINING MERCURY AND LEAD

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ABSTRACT. Treatment studies have been completed on an aqueous waste classified as land disposal restricted (LDR). The waste contained mercury and lead as characteristic hazardous constituents, while the primary radionuclide was Co-60. The primary objective of the treatment was to remove the characteristic hazard; removal of the nuclides was not required for successful treatment. Samples were treated by decanting, filtering, and then ion exchanging with Duolite GT-73. Effluent levels as low as to 0.003 mg/l mercury and 0.025 mg/l lead were obtained. Treatment was successful in that the LDR waste was rendered to forms for which ultimate disposal is available. The effluent water is suitable for disposal at the onsite warm waste ponds. The resin and solidified sludges passed the toxic characteristic leaching procedure and are suitable for disposal at the low-level burial grounds.

INTRODUCTION

The decommissioning of several nuclear reactors at the Idaho National Engineering Laboratory (INEL) has resulted in the generation of wastewaters containing both radioactive and toxic heavy metals. This type of waste form is not suitable for disposal at any landfill site and is, therefore, termed land disposal restricted (LDR). A program is currently under way at the INEL to establish treatments for these wastes so permanent disposal is possible.

The basic treatment approach is to remove the hazardous metals to below the Resource Conservation and Recovery Act (RCRA) limits and thereby render the wastewater as simple low-level waste. This water can then be disposed of at onsite evaporating ponds. The currently preferred treatments are precipitation and/or ion exchange. Any sludges or resins remaining after the primary treatment are also subject to the same restrictions as the original waste. For example, ion exchange resins must meet leaching requirements for toxic metals or they would themselves be classified as a mixed waste.

Two waste streams comprising a total of about 1,800 gal were the subject of recent treatment studies. The wastewater contained mercury and lead as hazardous constituents, while the primary radioactive component was cobalt-60. The objectives of the laboratory work were (a) to determine a treatment scheme that would remove mercury and lead to below RCRA limits and (b) to determine if secondary wastes such as ion exchange resins and sludges would be acceptable for land disposal.

ION EXCHANGE STUDIES WITH SIMULATED WASTE (COLD STUDIES)

Recent studies at Savannah River indicated excellent mercury removal using Duolite GT-73 ion exchange resin (1). This is a polystyrene-based material with thiol functional groups (-SH). The manufacturer's literature indicates that in addition to mercury, this resin also has a strong affinity for lead (2).

A laboratory column was assembled to test the resin on a simulated waste containing mercury and lead. The purposes of the test were (a) to verify that the resin could remove lead in addition to mercury to the desired level, (b) to establish a flow rate that would give adequate contact time for efficient metals removal, (c) to determine the resin's effective loading capacity, and (d) to supply a source of saturated resin for testing by the toxic characteristic leaching procedure (TCLP).

The tests were conducted in a 1.5-cm ID glass column equipped with chemical resistant polypropylene and Teflon components. A variable speed, reversible pump with thick-walled Tygon tubing was used to pump the feed solution. An approximate 1-in. liquid level was maintained above the resin to ensure good distribution across the bed's cross section and to supply hydrostatic pressure to force solution through the bed. Downstream of the column, the liquid flow was monitored and controlled with a rotameter and precision stainless steel needle valve. Effluent samples were withdrawn through a short sampling line immediately below the column exit. These were later analyzed for lead and mercury by an inductively coupled plasma emission spectrometer. Figure 1 is a schematic diagram of the experimental facility.

Table 1 presents the operating conditions for the experiment. Seven liters of feed, prepared from a stock solution of mercury and lead, were initially sent through the column. Later analysis of the effluent revealed that breakthrough had not occurred, and thereafter, feed solutions were prepared and fed to the column in 1 L increments. The feed was relatively concentrated with mercury, because the actual waste had the potential to be similarly loaded. Figure 2 shows the effluent mercury and lead concentrations plotted against the total solution passed through the bed. The curve follows the typical breakthrough shape, an initial period when essentially all mercury and lead is being removed followed by a period of rapidly increasing metals content.

The breakthrough point is defined here as the concentration at which the mercury is above the RCRA limit of 0.2 mg/L. By inspection of Figure 2, this would occur after about 800 bed volumes (BV) of feed were processed. The corresponding resin loading would be about 125 g of metals (mercury plus lead) per liter of resin. The breakthrough curve is relatively sharp using flow rates of 11.5 to 12.5 BV/hr; little improvement is expected to be gained by adjusting the flow rate.

ION EXCHANGE STUDIES ON ACTUAL WASTE (HOT STUDIES)

The knowledge gained from the cold tests was based on an idealized waste that was well characterized with no hindrance from trace or unknown components. Tests on the actual waste were essential to determine if interference from precipitated matter, other competing ions, or different pHs could seriously affect treatment.

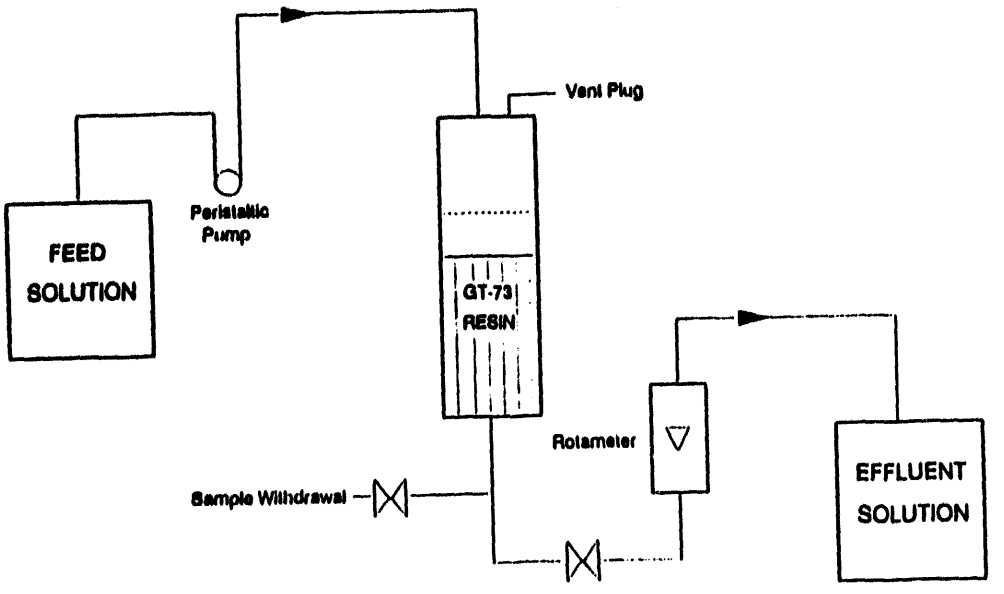

Figure 1. Schematic diagram of the ion exchange system.

Table 1. Operating conditions for the ion exchange experiments on simulated waste.

Feed solution:	
pH	7
Mercury	128 to 225 ppm Hg
Lead	6.7 to 7.8 ppm Pb
Flow rate	2.3 to 2.5 mL/min
	11.5 to 12.5 bed vol/hr
Bed characteristics:	
Resin	Duolite GT-73
Bed height	6.75 cm
Bed volume	12 mL

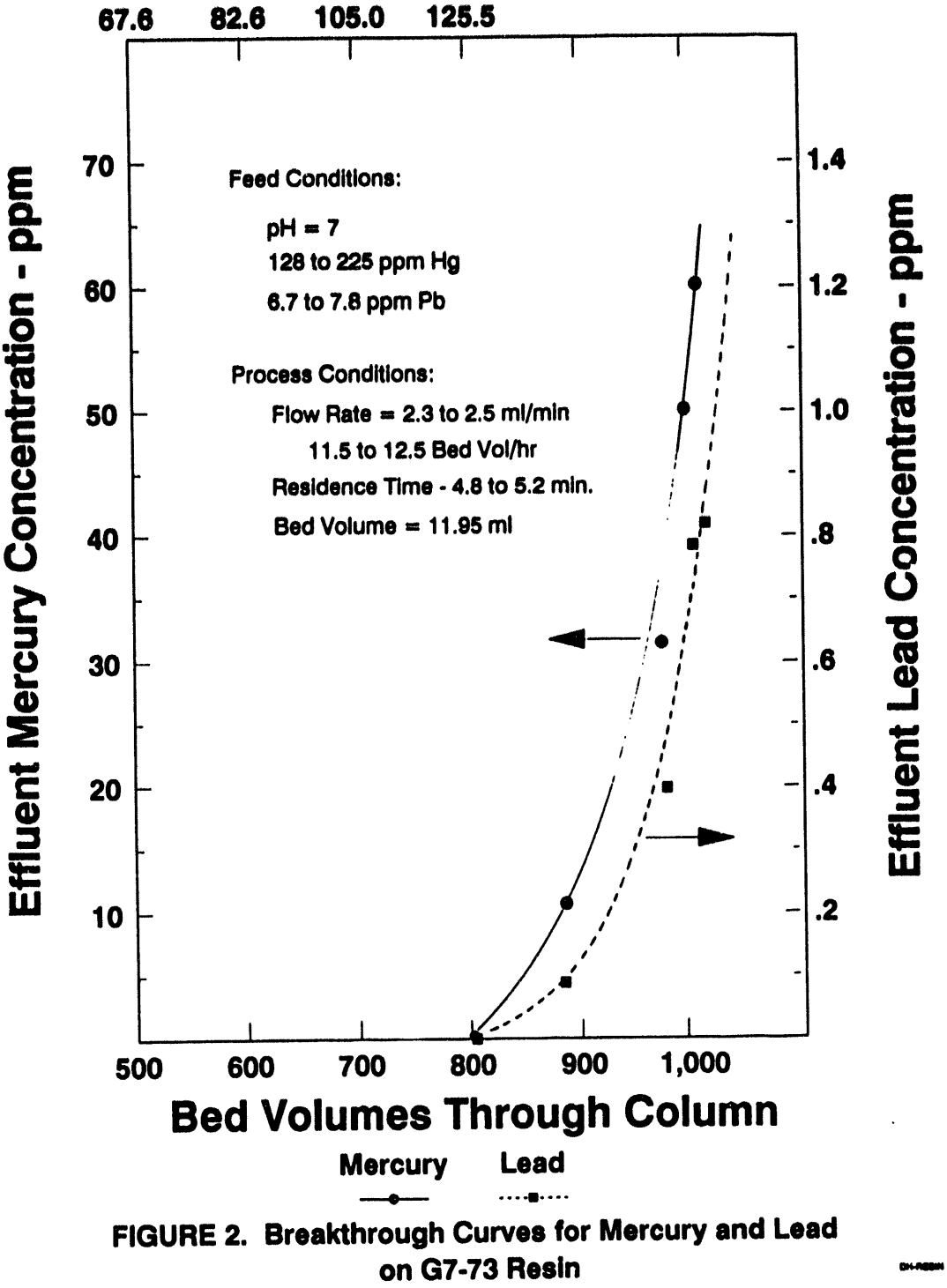

FIGURE 2. Breakthrough Curves for Mercury and Lead on G7-73 Resin

Figure 2. Breakthrough curves for mercury and lead on G7-73 resin.

History and Description of the Waste

The process knowledge of the waste is based on shipping records and descriptions from onsite personnel. Elemental mercury was used in a cooling jacket of an early experimental reactor. At the time of decommissioning, as much of the mercury as possible was removed by simple draining. Residual mercury was then dissolved and removed by recirculating a 30% nitric acid solution through the jacket. Caustic (NaOH) and then sodium sulfide were added to the solution to precipitate metals and to bring the pH up to about 10.

Thirty-three drums of this rinse waste were sent to the Mixed Waste Storage Facility in 1988. However, shipping records indicate that only 29 of the drums were actually processed as described above. The other four were originally labeled as corrosive and would, therefore, have a pH near or below 2. One of these four was later relabeled and was not shipped as a corrosive solution.

A sampling effort was initiated in which six of the 33 drums were sampled. Four of these samples were originally shipped as the processed waste, one was sent as corrosive, and the last was the drum with the altered designation. The six samples received by the laboratory were analyzed for hazardous components as well as radionuclides. Tables 2 and 3 are summaries of some of these results.

The first four drums listed in the tables were sent as the processed rinse water. Each sample contained a dark brown, fine-grained sediment that took several days to settle, leaving a clear liquid phase that was yellow to light brown. Most of the mercury and lead resided in precipitated form and could be removed by decanting and filtering; however, enough mercury remained soluble to be in excess of the RCRA limit. Only one of these four had lead above the RCRA limit of 5.0 mg/L.

The fifth entry, drum 703, was originally labeled as corrosive, but as is obvious from the data in Table 2, this was most likely a labeling error. This sample also contained a fine, brown sediment that settled to give a light brown liquid phase. The final entry, drum 702, was the rinse solution that was shipped as corrosive material. This sample was clear with only traces of sediment.

Several of the results in Table 2 are noteworthy. The dissolved metals content varied widely between samples, illustrating the highly inhomogeneous nature of this waste stream. The major background constituent was sodium, with its level ranging as high as 5 wt%. The acidic sample held most of the metals in solution and the corresponding lead and mercury levels were very high.

Table 2. Analytical results of the drum samples.

Drum number	pH	Filterable solids (mg/ml)	Dissolved solids (mg/ml)	Dissolved mercury (ppm)	Dissolved lead (ppm)
568	10	954	223	0.326	0.622
572	10	612	16.6	0.133	0.674
635	10	782	3.9	4.68	2.88
697	10	277	264	0.340	8.10
703	7	422	89.6	0.301	2.87
702	2	4.0	3.2	~20,000	~1,100

Table 3 shows the radiological information for the waste. The gamma analysis was performed on the raw waste samples. Gross β was determined separately for the filtered water and for the solids retained on the filter. Results indicate that most of the activity resided in the solids and sludge. No α-emitting nuclides were detected.

Table 3. Radiological analysis of drum samples.

Drum number	Solids gross β (pCi/g)	Liquid gross β (pCi/ml)	Gamma analysis (pCi/ml) Co-60	Ag-108	Cs-137
568	2.0×10^4	74	240	1.22	0.215
572	1.1×10^3	0.65	79.7	0.575	0.100
635	4.9×10^3	2.2	188	3.23	-
697	4.0×10^4	3.7	185	0.859	-
703	7.1×10^3	2.7	164	0.918	-
702	1.0×10^4	44	22.6	0.170	-

Treatment and Experimental Results on the Alkaline Waste

All the alkaline samples were combined into a single container, filtered, and then immediately passed through the ion exchange column. The feed conditions and column operating parameters are given in Table 4. The effluent retained only a slight yellow discoloration compared to the lemon color of the feed. There was also a pH drop of about 1.5 units on passage through the resin. The effluent was collected in a single container from which samples were drawn and sent for metals and radionuclide analysis. Validated data results show that mercury levels were reduced to 3 μg/l, while lead was at about 25 μg/l. The corresponding RCRA limits are 200 and 5,000 μg/l, respectively. Co-60 levels in the effluent was determined to be 2.27 pCi/ml, while no detectable levels of Ag-108 were found. There are no established disposal limits for radioactive materials, although the U.S. Department of Energy (DOE) does give derived concentration guidelines (DCG) for worker exposure and ingestion (3). The level of Co-60 was below the 5.0 pCi/ml DCG for worker ingestion of the water.

Table 4. Feed and operating parameters of the ion exchange treatment of alkaline wastes.

Feed solution:	
pH	10
Mercury	1.2 ppm
Lead	3.0 ppm
Flow rate	5.5 to 5.9 ml/min
	9.6 to 10.3 bed vol/hr
Bed characteristics:	
Resin	Duolite GT-73
Bed height	19.5 cm
Bed volume	34.5 ml

Treatment and Experimental Results on the Acidic Waste

The large-scale treatment of this waste was to be performed at a unit that requires the feed to have a pH above 6. This constraint guided the laboratory handling of the waste. The initial treatment was to adjust the pH to about 9-10 by adding a 50 wt% NaOH solution. This caused much of the dissolved metals to precipitate. The resultant hydroxides readily settled and allowed very easy decanting and filtering of the lighter liquid phase. Analysis of this liquid showed very significant mercury and lead levels at 166 and 94 mg/l, respectively. Because of this high loading, the solution was passed through the resin column twice. The feed flow rate was again maintained at about 10 BV/hr. Analysis of the effluent showed that mercury and lead were removed to 143 and 76 μg/l, respectively. The Co-60 activity was reduced to 0.16 pCi/ml.

Wastes Generated from Primary Treatment

Any material used or generated in the treatment of a hazardous, mixed waste is subject to the same scrutiny as the original waste. The ion exchange resin and sludges are considered radioactive because they were used or emanated from a radioactive waste stream. To be classified as a simple low-level waste, they would have to pass the TCLP tests for metals, or otherwise they would be classified as a mixed waste.

Duolite GT-73 was used exclusively throughout these tests and at the conclusion, a sample of the resin was sent for the TCLP test. The mercury and lead leachate levels were 14 and 1,100 μg/l, respectively. These are below the RCRA limits and this material is, therefore, considered a low-level waste and can be disposed of at the onsite burial grounds. A gamma scan of the resin also showed the resin to retain Co-60.

Two types of sludges were available from the laboratory studies—mercury and lead sulfides from the onsite processed rinse water and the hydroxide precipitates of the same metals from the acidic waste neutralized in the laboratory. Because the solubility of sulfides is generally much lower than hydroxides, a sample of the sulfide material was sent for TCLP testing. Results indicate that mercury bound as a sulfide would pass the leaching requirement, but lead will not. The sludges would, therefore, be considered a mixed waste and may not be disposed of at the burial grounds. These were later solidified in hydraulic cement, which was also subjected to TCLP testing. The solidified material was found to retain the metals in a stable, nonleachable form and can be disposed of at the onsite burial grounds (3).

SUMMARY

The laboratory studies described in this work were highly focused on the treatment of a specific waste stream, however, the information can be generalized to be of interest to those dealing with similar wastes. The laboratory results verified that under alkaline and neutral conditions, Duolite GT-73 resin will remove mercury and lead to levels well below RCRA limits and will approach or even exceed drinking water standards, despite a high sodium background. This was achieved by maintaining flow rates of about 10 to 12 BV/hr. The resin's effective capacity was estimated at 125 g of metals (as mercury plus lead) per liter of resin. This value was established under controlled conditions and should be viewed as a maximum value.

Two secondary wastes were generated during the course of primary treatment. The resin was subjected to TCLP tests and was found to retain lead and mercury adequately enough to meet RCRA leachate limits. Sulfide and hydroxide sludge were also generated. The sulfides, having a lower solubility than the corresponding hydroxides, were considered the most likely to pass the TCLP requirement and were subjected to the test. The leachate from the sulfide sludge met the mercury standard but failed for lead. All sludges were, therefore, considered a mixed waste and were stabilized by grouting in hydraulic cement.

The laboratory studies were used to design and successfully treat about 1,800 gal (33 drums of 55 gal) of onsite mixed waste. Thirty drums were neutral or of alkaline pH and were processed by decanting, filtering, and then ion exchanging. The final three drums, which were originally acidic, were pH adjusted with caustic and then processed like the other thirty.

ACKNOWLEDGMENTS - This work was supported by the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, under DOE Idaho Field Office Contract DE-AC07-76ID01570.

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BIOPROCESSING SCENARIOS FOR MIXED HAZARDOUS WASTE

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ABSTRACT. The potential of biological processing of mixed hazardous waste has not been determined. However, the use of selected microorganisms for the degradation and/or detoxification of hazardous organic compounds is gaining wide acceptance as an alternative waste treatment technology. The isolation of a unique strain of *Pseudom ovos Putida Idaho* seems well adapted to withstand the demands of the input stream comprised of liquid scintillation waste. This paper describes the results from the continuous processing of a mixture comprised of p-xylene and surfactant. The process is now at the demonstration phase at one of US Department of Energy's facilities which has a substantial amount of stored waste of this type.

INTRODUCTION

In 1993, the International Atomic Energy Agency convened a technical committee meeting to discuss wastes emanating from the nuclear fuel cycle. During this multi country technical discussion, several issues became evident. Low and intermediate radioactive waste in general are being stored in a process that is called cementation. Some of these wastes contain quantities of organic materials. The organic matrices are not always compatible for the cementation. Therefore, new technologies or existing technologies which can be adapted are being sought to solve the problems before long term or interim storage packaging occurs.

Biotechnology offers a role as a technology for waste treatment. Previous treatments only sought technologies from chemical and physical methods. Today, the progress in environmental biotechnology especially in the degradation of a myriad of organic chemicals as well as a separation of metal ions makes it an excellent candidate for some of the nuclear waste problems. In some cases, biotechnological methods will be part of a processing chain to accomplish the goal. In other situations, bioprocessing may achieve organic degradation while accomplishing a nuclide separation.

During the first symposium on this subject, we discussed the continuous processing of waste xylene via a microbial process. Since that event, a substantial increase in knowledge has been gained regarding the uniqueness of this organism. We believe this organism may be an excellent host to insert additional catabolic pathways for the degradation of other organic components of mixed wastes, e.g. turbine oils, benzene, dioxane, tributyl phosphate. This paper reports on the work that our lab and David Gibson's lab at the University of Iowa have accomplished over the last two years (1).

METHODS AND MATERIALS

Batch Experiments

Cultures of *Pseudomonas putida Idaho* (PpID) used in batch experiments designed to determine effects of solvent concentration and utilization as well as solvent-induced physiological effects were maintained in mineral salts based medium (MSB). P-xylene or toluene was added directly to the liquid MSB medium at 5% u/v or flooded (5mL) on plates of MSB medium solidified with 1.5% agar. Resistance to the effects of high concentrations of organic solvents was measured in Luria-Botani (LB) medium. The total volume of medium plus solvent was 25% of the culture flask.

Chemostat Experiments

The primary reactors were modified New Brunswick Multigen Fermentors. Modifications allowed for the injection of neat p-xylene directly into the first reactor (Br1) below the level of liquid, and the reactor contents were pumped to the second reactor, see schematic (Fig. 1). Effluent from Br1 was used as feed for the second reactor (D2). Any liquids which contained p-xylene were pumped through glass or viton tubing, which was shown to be highly impermeable to p-xylene. The heads of the reactors were machined out of teflon. During each change of a variable, a 2.5 day adjustment period was allowed to achieve steady state conditions before additional data were taken.

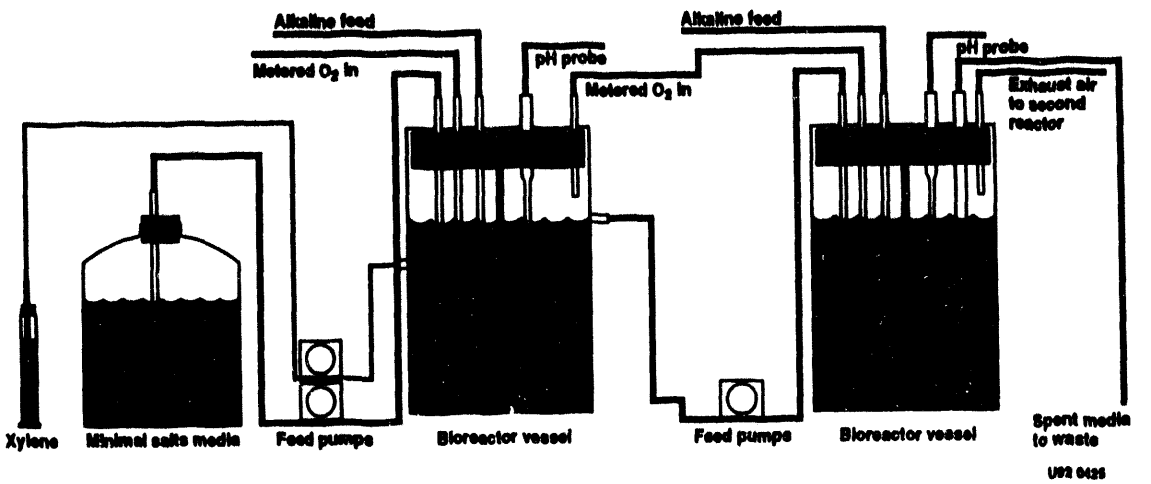

Figure 1. Feed stream configuration for bioreactor system.

Mass Balance Determinations

To quantify the concentrations of p-xylene in the feed and effluent streams for the reactors in both aqueous and vapor phases, a gas column injector was used. Total carbon was analyzed with a total organic carbon (TOC) analyzer. Samples for carbon balance were directly injected into the instrument and analyzed for

total inorganic carbon (TIC), total purgable carbon (POC) and TOC. Air samples were taken by absorbing p-xylene from exiting air of the chemostat onto charcoal traps. Contents from the trap were desorbed with 5 ml of carbon disulfide and an aliquot was then analyzed by GC (Fig. 2).

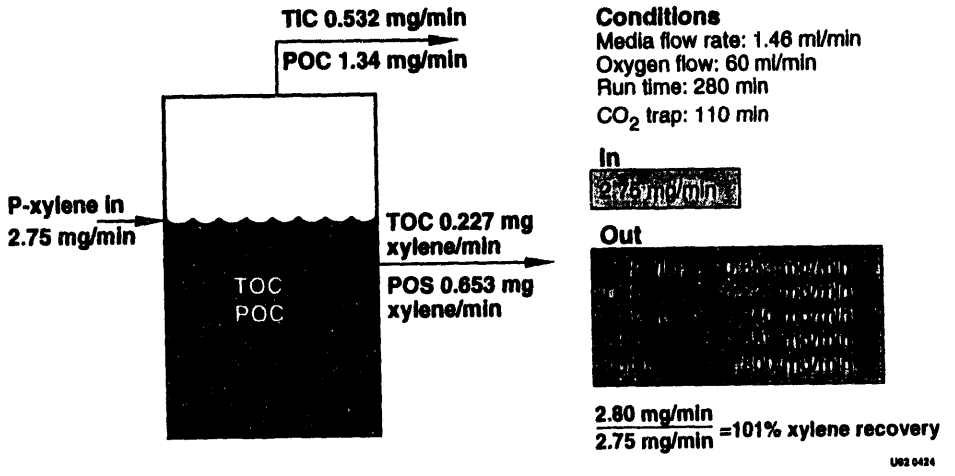

Figure 2. Mass balance of carbon as p-xylene.

RESULTS AND DISCUSSION

Batch Studies

Ultrastructure of PpID. Thin sections of succinate-grown PpID cells under scanning electron microscopy (SEM) show the ultrastructure typical of pseudomonas. However, when cells are grown with p-xylene vapors the outer membrane in convoluted and in places clearly separated from the cytoplasmic membrane. Inclusion bodies different from those in succinate-grown cells are present. When cells are grown with 20% v/v p-xylene, the outer and cytoplasmic membrane are separated and convoluted, and the cytoplasmic membrane, especially appears disorganized. Electron dense inclusion bodies are still present and fragments of the outer membrane appear to be shed into the medium. This work was performed in David Gibson's laboratory.

Solvent Tolerance. The ability of PpID to grow on LB medium in the presence of a range of organic solvents was determined (Table 1). Solvents are listed by decreasing hydrophobicity expressed as the logarithm of the octano-water partition coefficient (Log P_{oct}). Of the solvents listed, only toluene and p-xylene could be used as growth substrates. Abundant growth was observed on LB plates when the surface of the agar was flooded with solvents that have a Log P_{oct} equal to or greater than 2.3. However, both tolerance and utilization only occurred in the presence of p-xylene and toluene. In this case only, MSB agar was used which did not contain any additional carbon substrates. Growth still occurred within 48-72 hours after streaking the plate and flooding it with p-xylene. No other Pseudomonas strain tested was able to tolerate organic solvents to the same extent as PpID.

Location of Genes Including P-xylene Degradation. Attempts to detect the presence of a catabolic plasmid in PpID were not successful. These studies and hybridization work have shown that the genes encoding enzymes for the degradation of p-xylene, m-xylene, and toluene are located on the PpID chromosome. This work was performed in David Gibson's laboratory.

Table 1. Growth of *P. putida Idaho* in the presence of organic solvents[a]

Solvent	Log P_{OCT}[b]	Growth[c]
n-Decane	5.6	+++
n-Octane	4.5	+++
Cyclooctane	4.1	+++
n-Heptane	4.0	+++
1-Octene	3.7	+++
Propylbenzene	3.6	+++
n-Hexane	3.5	+++
Diethylphthalate	3.3	+++
Cyclohexane	3.2	+++
Ethylbenzene	3.1	+++
p-Xylene	3.1	+++
n-Pentane	3.0	++
Styrene	3.0	+++
1-Octanol	2.9	+++
Cyclopentane	2.5	+++
Toluene	2.5	+++
1,5-Hexadiene	2.5	++
1-Heptanol	2.4	+++
Dimethylphthalate	2.3	+++
Fluorobenzene	2.2	-
Benzene	2.0	-
Chloroform	2.0	-
1-Hexanol	1.8	-
1-Butanol	0.8	-

[a] Cells were grown in LB medium in the presence of 25% (vol/vol) solvent as described in Materials and Methods.

[b] Calculated from hydrophobic fragmental constants in Laane et al. (21) and from values in Rekker and deKort (27).

[c] Symbols indicating turbidity values at 600 nm: +++, >1 after 24h; ++, 0.7 to 1.0 after 48 h; -, <0.2 after 48 h.

Continuous Flow-Degradation Studies

The sequential bioreactor system was modified to provide a closed system from which mass balance studies could be obtained (Fig. 2). This system served as the apparatus to evaluate a method for the continuous utilization of p-xylene. During its use, various parameters were evaluated to provide engineering data necessary for process scale up. During the two years that this system was operated re-inoculation was never necessary. Even with pH excursions from 2-11, after re-stabilization of the conditions, the cell density would again increase and steady state conditions could be maintained.

Aeration Conditions. A flow rate of 60 mL/min of pure O_2 into the 1.5 L reactor vessel (working volume of 1 L) was determined to be optimum. The efficiency of the method (as determined by p-xylene degradation) at various O_2 flows was determined (Fig. 3). Several factors played a role in this conclusion. Insufficient oxygen caused detrimental effects on the cell population in the reactor, while excessive aeration caused the volatile organic to be swept away from the dissolved phase and shorten its retention time in the reactor. In Fig. 4, the effects of adding different flows of oxygen are displayed. At the lowest feed rate of 50 mL/min, only 0.3 mg/min of p-xylene was stripped into the vapor/phase while a four fold increase in O_2 flow resulted in more than ten times that amount of p-xylene stripped.

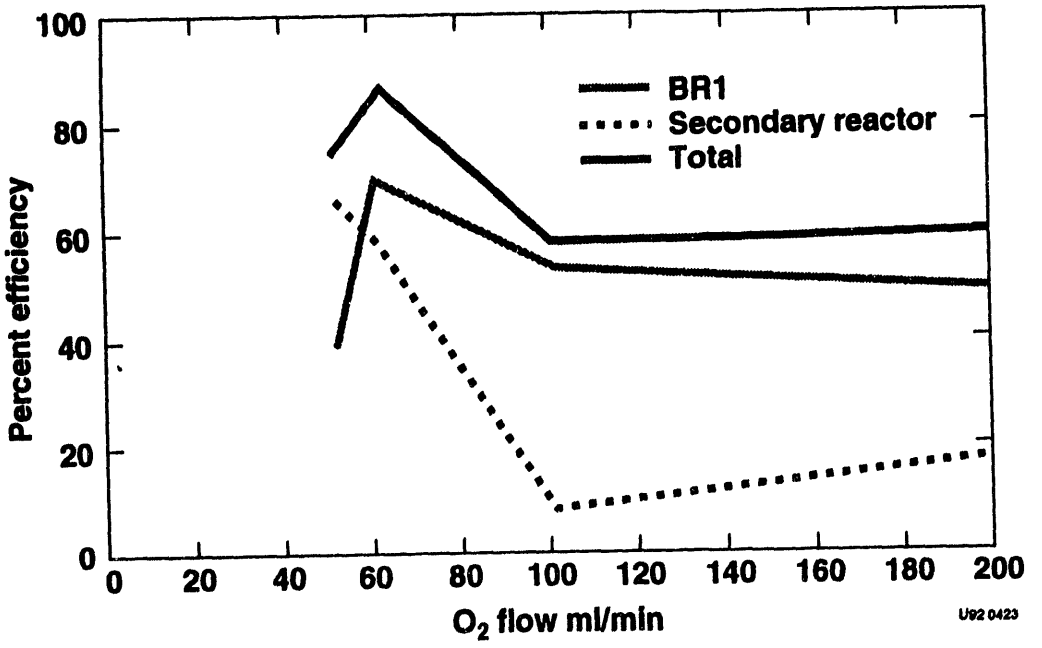

Figure 3. Reactor efficiency at different O_2 flows.

Flow Rates. In order to determine the through put of the reactor, a series of flow rates of mineral salts media were introduced into Br1 with a p-xylene flow rate maintained at 4.0 mg/min. Each flow rate was run for four days or longer. The data from each media flow rate study was averaged and are shown in Fig 5. Two observations were noticed. First, a four-fold increase in media did not cause cell washout or a substantial decline in degradation efficiencies in the reactor. Secondly, an overall degradation efficiency of 90% or greater was maintained.

The maximum flow rate used in this study resulted in a retention time per reactor of approximately three hours. The concentration of p-xylene in the feed stream was 2,700 ppm at the lowest flow and 770 ppm at the higher flow rate. Both the short retention time and the level of substrate feed were better than previously described for other continuous degradation studies (2,3).

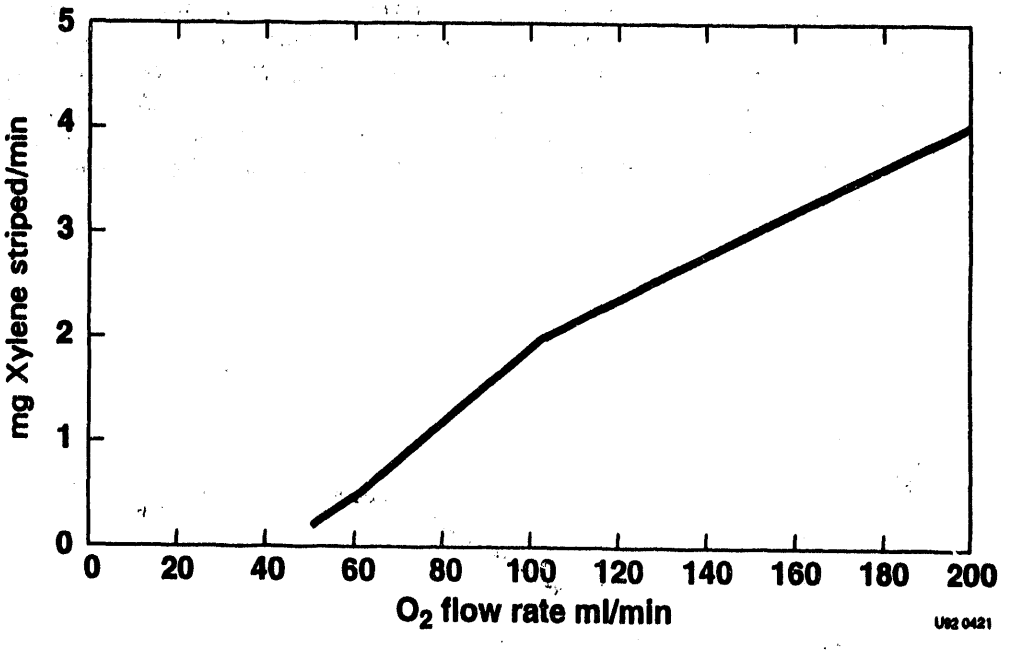

Figure 4. Xylene stripping at different O_2 flows.

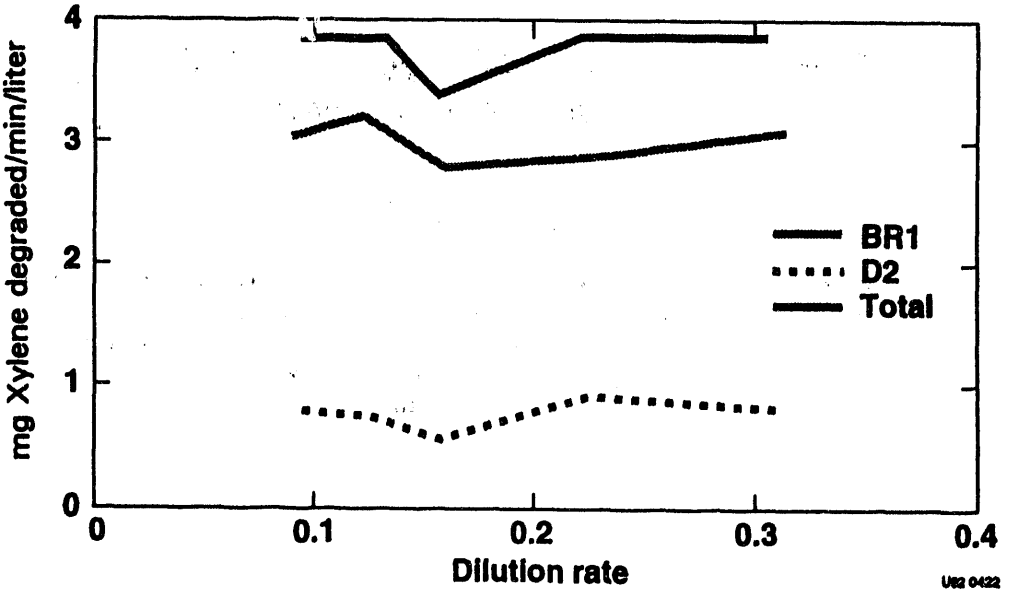

Figure 5. Xylene degraded vs. dilution rate.

Concentration of Substrate Feed. The concentration of p-xylene feed was increased and the degradation rate was determined for each loading rate. During this series of tests, the flow rate of media was held constant at 4.15 mL/min. In Fig. 6, the results of this series of experiments are shown. The optimum degradation rate achieved was greater than 6 mg/min/L at a feed rate of 20-28 mg/min of p-xylene.BioProcess Demonstration Project. The current inventory of liquid scintillation waste at the Department of Energy (DOE) facilities is listed in Table 2 (4). Present production figures for each facility and the type of radio-nuclide in the stored waste are all unknown. Other commercial sources are also producing mixed wastes of this type. Although recent scintillation cocktail formulations are biodegradable, in the future these mixtures may not be considered non-toxic. Past cocktail formulations gave good counting efficiencies and good emulsion characteristics. If processes can be developed to handle these formulations which were composed of small chemical molecules containing non-stearic hindered substituted side-chain groups, the reformulation of scintillation counting liquid with complex molecules could be avoided.

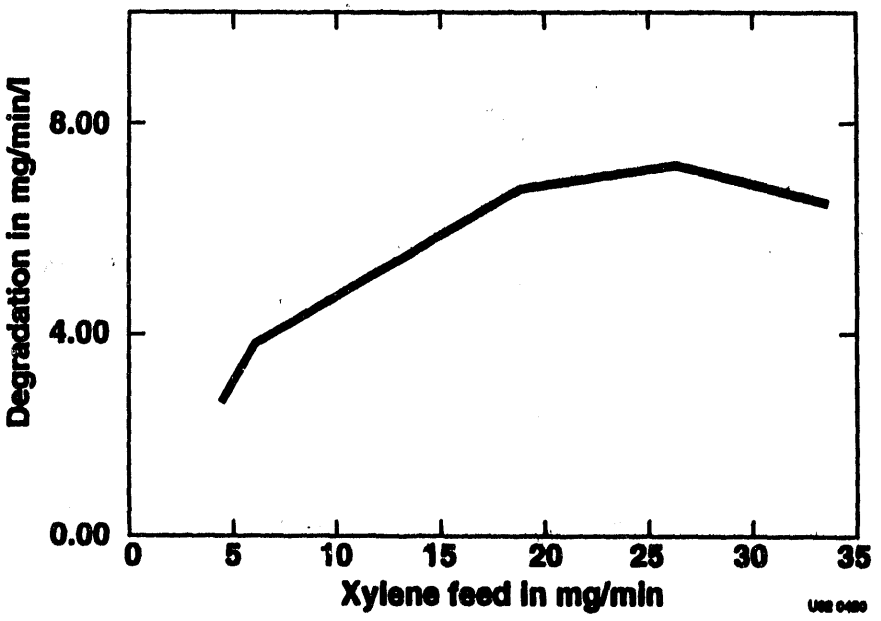

Figure 6. Degradation rate vs. xylene feed BR1.

The DOE Mound facility is the site for the demonstration of this process. The current status for this project is that it is under way and the reactors were set-up in March 1993. A radiological lab was made available for the testing phase which will include reactor start-up, inoculation, tests with non-radioactive p-xylene cocktail mixture, 14 c-toluene tests, and spiked tritium and plutonium studies. The testing will culminate in the processing of some stored waste under permitted conditions.

Table 2. Quantities of Liquid Scintillation Waste in the DOE System[1]

Site	Generation Rate (gals.)/year	Quantity Stored (gals.) 12/31/90
BNL	792 (3)[2]	448 (1.7)[2]
GJPO	5 (0.02)	1 (0.01)
INEL	0 (0)	55 (0.21)
PTX	792 (3.0)	1230 (4.66)
ANLE	0 (0)	1330 (5.04)
BWL	1122 (4.25)	3300 (12.5)
FMPC	0 (0)	5 (0.02)
LANL	1320 (5)	11866 (44.95)
LBL	0 (0)	1003 (3.80)
LLWL	264 (1)	NK
MND	169 (0.64)	10480 (39.7)
ORNL	1494 (5.66)	839 (3.18)
PPPL	5 (0.02)	5 (0.02)
SNLL	84 (0.32)	166 (0.63)
SRS	396 (1.50)	1188 (4.50)
WVDP	0 (0)	1 (0.01)
Total	6443[3] (24.41)	31862 (120.72)
Estimated Disposal Cost[4]	$8,718K	$43,114K

1. WMS Data Base (Tim Kirkpatrick, INEL)
2. Volume M^3
3. This total represents 1% of the total US production of LSW based on the California Model of Mixed Hazardous Waste Production.
4. Estimated at $357 to $536K per M^3 by the Central Interstate Compact (J. K. Krieger, in Radioactive Exchange, September 9, 1991).

SUMMARY

In summary, an isolate has been identified that appears to have unusual capabilities for surviving and growing under chemostat conditions with high concentrations of p-xylene and in the presence of high levels of surfactant. This is a unique discovery in that the isolate reported by Inoue and Horikoshi (5) could only tolerate high concentrations of toluene but could not metabolize toluene. The results gained from these tests and the demonstration taking place at the Mound Facility in Ohio, will provide the mathematical evaluation

necessary for the development of a pilot scale, harden engineered system. This processing system will also allow the development of mobile and stationary systems for in-line and end-of-pipe treatments of selected industrial waste streams. The inventory of stored liquid scintillation waste in the DOE system is shown in Table 2 and is a result of a recent survey.

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CHAPTER 15

TSD Facility Design

DESIGN OF THE WASTE RECEIVING AND PROCESSING MODULE 2A FACILITY

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ABSTRACT. Westinghouse Hanford Company has determined that a facility is required for the treatment of mixed low-level waste at the Hanford Site. The mission of that facility will be to receive, process/treat, package, certify, and ship the contact-handled, mixed low-level waste that must be handled by Hanford Site to permanent disposal. Preconceptual and conceptual design studies were performed by United Engineers and Constructors, and a conceptual design report was issued. This report presents a summary of the conceptual design for a facility that will meet the mission established.

INTRODUCTION

The proposed Waste Receiving and Processing (WRAP) Facilities would provide treatment for radioactive solid wastes at the U.S. Department of Energy, Richland Field Office's (RL) Hanford Site. The current planning is for the WRAP Facilities to be constructed in complementary modules; each will be provided by separate projects. The proposed 1994 Project W-100 will provide WRAP Module 2A, which is a facility for the treatment of mixed low-level waste (MLLW).

The function of WRAP Module 2A is to provide nonthermal treatment of contact-handled MLLW required for disposal at the Hanford Site. Since 1987, when the Resource Conservation and Recovery Act of 1976 (RCRA) (1) was applied to U.S. Department of Energy facilities, MLLW has been stored at the Hanford Central Waste Complex, awaiting a treatment capability to permit permanent disposal of low-level waste compliant with land disposal restrictions. MLLW volume currently stored and forecasted to be generated over the next 30 years totals approximately 23,220 m^3 (820,000 ft^3), of which 17,840 m^3 (630,000 ft^3) does not require thermal treatment for disposal. This waste is designated to be stabilized/immobilized in WRAP Module 2A.

WRAP Module 2A will accept waste packages that are contact handled and designated as MLLW category 1 or MLLW category 3, according to Westinghouse Hanford Company designations. Before receipt, all of the waste received at the facility will be characterized for dangerous and radionuclides constituents, according to Washington Administrative Code (WAC) 173-303 (2) and other regulations. MLLW shall be treated, in accordance with WAC 173-303 to stabilize/immobilize the waste by either cementitious grout or polymer, deactivate any reactive metals, and encapsulate lead and lead products and amalogate mercury and mercury products. Specialty waste like mercury, lead, and reactive metals that require special processing shall be held in storage for campaigning in a separate specialty process enclosure provided in WRAP Module 2A.

The facility will handle incoming 208-L (55-gal) drums, 314-L (83-gal) overpacks containing 208-L (55-gal) drums, 416-L (110-gal) drums, and boxes up to 1.5 m by 1.5 m by 2.8 m (5 ft by 5 ft by 9 ft). The boxes

will be handled in a separate box breakdown area where the waste is size reduced to be placed in a 208-L (55-gal) drum and handled accordingly. All outgoing treated wastes shall be packaged into new 208-L (55-gal) drums for onsite disposal.

WASTE FEED DESCRIPTION

The waste sources to be treated in WRAP Module 2A include secondary solids from Hanford Site liquid effluent treatment facilities (LETF), thermal treatment facility ash, other WRAP modules, storage, and onsite and offsite waste generators. The WRAP Module 2A Facility shall receive waste in boxes and drums. All Module 2A-treated waste shall be packaged into 208-L (55-gal) drums and assayed, as needed, to certify the low-level waste category, and then disposed of at a RCRA-approved low-level waste trench located at the Hanford Site.

Table 1 contains the summary information on the waste that has been identified for treatment in WRAP Module 2A. The table contains the source of the waste by generator, general waste type, major chemical characteristics, hazardous components, estimated volume, selected treatment process, and the production rates through WRAP Module 2A.

Table 1. WRAP module 2A Waste Treatment Strategy Summary.

Waste Source	Waste Type	Major Chemical Species	Hazardous Component Requiring Treatment	Projected Total Inventory, m^3 (ft^3)	Annual Feed Throughput, m^3 (ft^3)	Treatment Process	Annual Production Output, Drums
183-H Solar Evaporation Basins in storage	Sorbond liquids	Sodium nitrate	Chromium, mercury, cadmium, silver barium	2,489 (87,912)	100 (3,525)	Polymer	999
	Crystalline solids	Sodium sulfate					
	Sludge	Copper sulfate					
	Miscellaneous cleanup	Contaminated debris		268 (9,471)	11 (385)	Grout	53
Liquid effluent treatment facilities forecast	C-018 Evaporator salt cake	Ammonium sulfate	Chromium, mercury, nickel	7,844 (277,000)	357 (12,600)	Polymer	3,288
	Ion exchange resins	Nitrates and radionuclides					
	L-045 Metal sludge	Heavy metal hydroxides	Chromium, mercury	2,124 (75,000)	96 (3,400)	Grout	873
	RO Filter elements	Contaminated debris					
Operations in storage and forecast	Dry active waste	Contaminated debris	Debris waste	1,843 (65,100)	92 (3,255)	Grout	443
	Construction debris						
	Metal wastes	Lead, mercury, reactive	Lead, mercury	609 (21,500)	Varies*	Polymer	Varies*
	Absorbed chemicals	Noncombustible adsorbents	Inorganics and heavy metals	963 (34,000)	48 (1,700)		495
Thermal Treatment Facility forecast	Incinerator ash	Heavy metals	Chromium, mercury, barium, cadmium, lead, silver, selenium	1,688 (59,600)	84 (2,980)	Grout	809
Retrieval forecast	Contaminated soils						

*Metal waste is campaigned. Throughput varies with campaign length and waste volume.

FACILITY LAYOUT

The facility layout was established during the conceptual design effort performed by United Engineers and Constructors in Englewood, Colorado. Figure 1 is the plan view of the facility as defined in the conceptual design report (3).

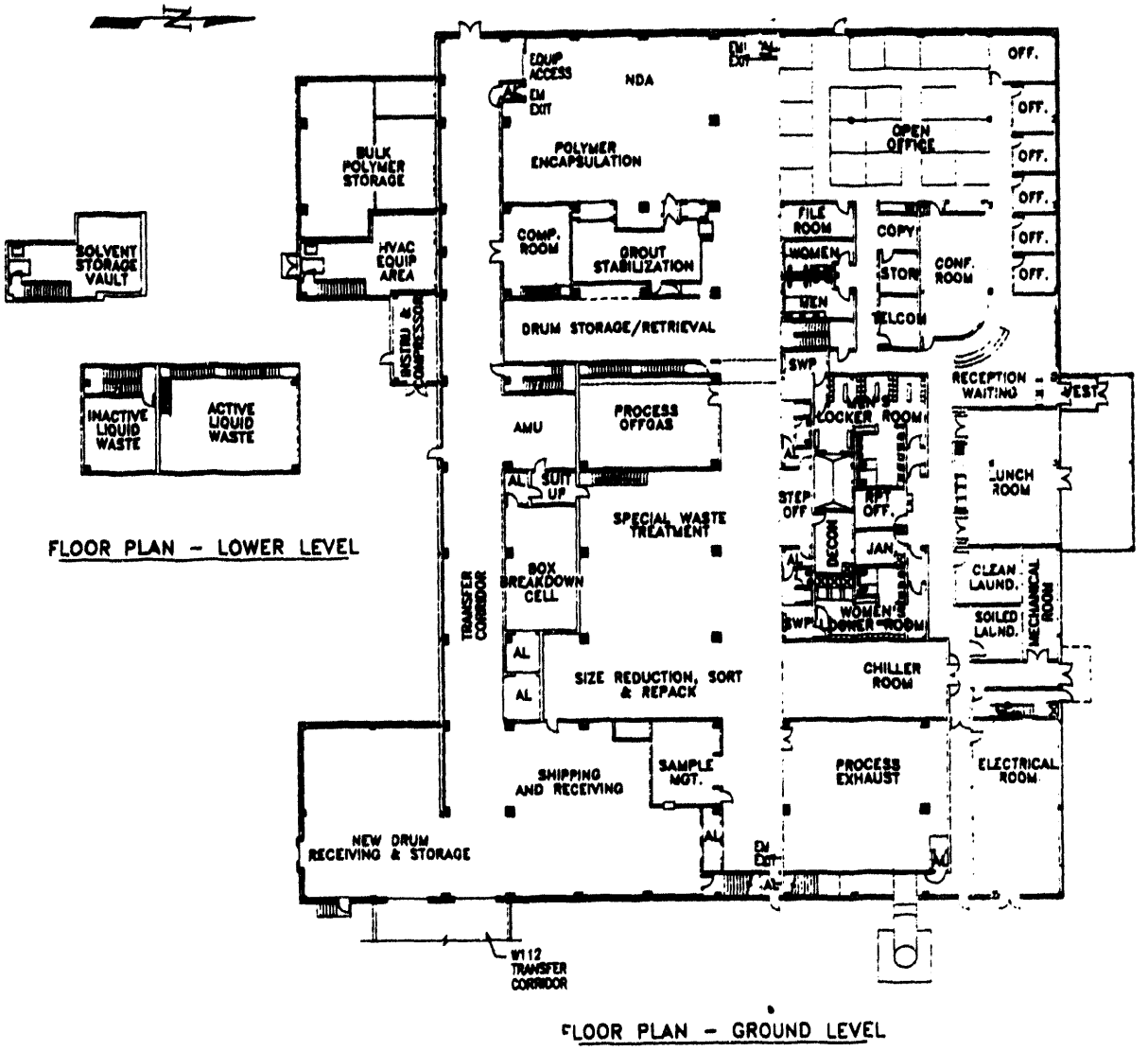

Figure 1. WRAP 2A Conceptual facility layouy plan.

TREATMENT PROCESSES

The following sections describe the treatment processes and functions proposed to be provided in the current conceptual design of the WRAP Module 2A Waste preconditioning, an agitated cement-based grout process, an agitated thermosetting polymer immobilization process, a vibratory cement-based grout process, and a vibratory thermosetting polymer immobilization process are the basic mixed waste treatment processes available in WRAP Module 2A. Treatment of lead and mercury are also provided. Figure 2 provides a schematic of the major processes contained in WRAP Module 2A.

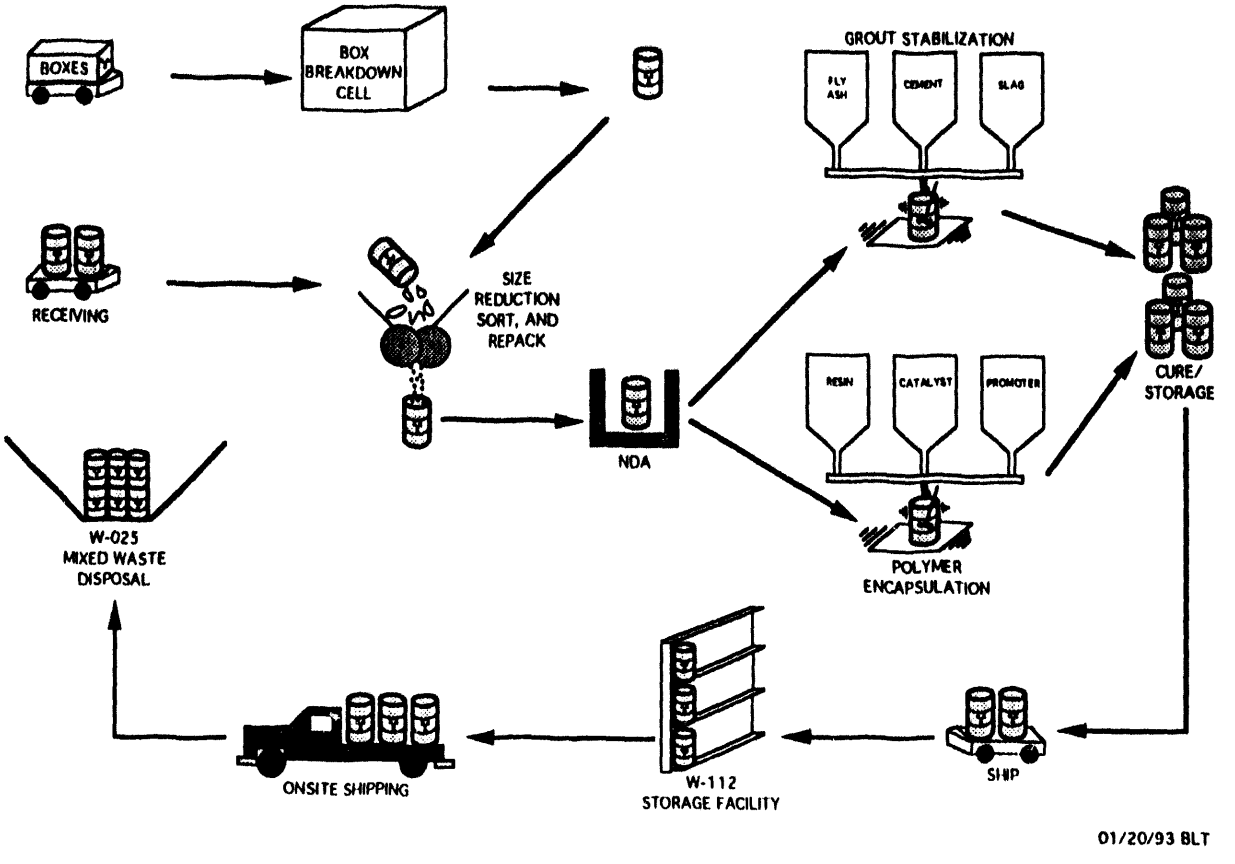

Figure 2. WRAP module 2A material flow.

Precondition the Waste

The preconditioning step for all waste entering WRAP Module 2A is to open each container, to place the waste onto a sorting table/conveyor system, and to inspect the waste for noncompliant items. This allows the waste to be repackaged into the final waste disposal container in the correct amount to allow immobilization with the selected binder materials. Depending on the type of waste to be processed, the waste is passed through a shredder system for volume and size reduction or passed through a pug mill to homogenize the waste. The waste is then metered, by weight, into the final container in the preconditioning enclosure before the drum is placed in lag storage awaiting movement to the grout or polymer enclosures. A stacker/retriever drum storage device is provided to allow in-process lag storage for separation of the basic processes of preconditioning and immobilization of the waste.

Cement-Based Grout

The wastes identified to be immobilized in the grout process are those that contain small quantities of soluble salts or chemicals that could interfere with the solidification of grout. These wastes are mainly dry active waste or construction debris-type materials.

The bulk grout materials (blast furnace slag, portland cement, and pulverized fly ash) will be contained in large silos adjacent to the facility. The grout treatment area will be a cell-type process enclosure that will house the grout-filling equipment, grout cure storage, excess water inspection, and drum decontamination. To prevent contamination, efforts were made in the design to keep the major portion of equipment outside the enclosure. The grout process uses in-drum mixing of the grout and the waste. The two in-drum mixing techniques that are used to mix the grout and the waste are (1) an agitated or stirred mixing process, and (2) a vibratory mixing technique. Both methods are accomplished in the same enclosure and at the same fill station.

Agitated Cement-Based Grout

The agitated or stirred mixing technique is used for particulate-type waste such as contaminated soils, ash, and dry salts. This waste is characteristically homogenous. The prefilled drums of waste and a paddle are first mixed with the water to obtain a slurry. The dry grout materials are preblended and then added to the agitated slurry in controlled quantities to obtain the required blend. The drums remain in the enclosure for 48 hours to allow for sufficient solidification and to permit inspection of the final product.

Vibratory Cement-Based Grout

The vibratory grout process is used on a different waste type. This waste type is characterized as "large pieces" of heterogenous waste consisting of irregular shapes and variations of physical features. This material most likely has been preconditioned by shredding. The waste is added to the drum without a mixing paddle. Stirring this waste type is difficult, and the vibratory process was selected as the best method to encapsulate the waste. The vibratory system involves using an external vibrating device to impart a vertical and horizontal oscillation to the drum to allow flow of the grout mixture to fill the voids within the waste matrix. The prefilled drums of waste are placed on a vibrating table, and premixed grout and water are added to the waste as the drum is vibrated. The drums remain in the enclosure for 48 hours to allow for sufficient solidification and final inspection.

Thermosetting Polymer Immobilization

Waste that is not suitable for grout encapsulation due to high soluble salts, ammonium sulfate, and other characteristics will be encapsulated in a thermosetting polymer. The thermosetting polymer process selected for WRAP Module 2A uses a three-part system consisting of a binder, a promoter, and a catalyst. The binder is a 50 percent polyester dissolved in styrene. The promoter is an aromatic amino compound such as dimethyl *p*-toluidine. Any two of the components can be mixed without causing polymerization. However, after the catalyst is added curing will start. Rapid curing occurs in two stages. The first occurs in 5 minutes to 1 hour, depending on the catalyst added. At this point the styrene has reacted and the mixture is stable. The second curing is an exothermic reaction. This reaction is marked by a rapid temperature increase of the polymer. Depending on mixing ratios in this reaction, peak temperature as high as 120 °C (250 °F) can occur between 30 minutes and 2 hours after catalyst addition. The curing and cool down period can last up to 48 hours. In WRAP Module 2A, each component is stored in individual tanks located separate from the facility. A separate tank located near WRAP Module 2A is used to premix the promoter and binder. The specific waste to be processed determines how the catalyst is added.

Agitated Thermosetting Polymer Immobilization

In the agitated thermoset process, as in the agitated grout, the waste with a lost paddle is placed into the drum during waste preconditioning. The premixed binder/promoter is pumped to the enclosure and introduced into the drum containing the waste and paddle. The waste is stirred until a homogenous mixture is obtained. The catalyst is then added as the mixture is continually stirred. After a period of time, mixing is stopped. The drums remain in the fill station for about 1 hour to allow the mixture to gel before the drum is removed. The mixture is allowed to gel before removing the drum from the fill station. The drums are moved to a separate isolated area to allow for the exothermic reaction to be completed.

Vibratory Thermosetting Polymer Immobilization

In the vibratory thermoset polymer process, the waste is placed into the drum in the preconditioning area. However, a paddle is not included in the loaded drums. The premixed binder/promoter and the catalyst are pumped separately to the process enclosures. In-line mixers just outside the enclosure mix the binder/promoter with the catalyst, and the mixture is then added to the waste drum as the drum is vibrated on the same type vibratory device used in the vibrated grout process. The mixture is allowed to gel before removing the drum from the fill station. The drums remain in the fill station for about 1 hour to allow for sufficient solidification before drum movement.

Special Waste Processes

A separate process enclosure is provided to precondition special waste before introducing the resultant waste into the grout or polymer immobilization processes. Special waste is waste that contains quantities of lead or mercury, either as a contaminate or as elemental metal. Contained within the special waste process enclosure is a sorting table to separate items that do not require special treatment. After sorting, mercury-contaminated solids are shredded and moved into a mercury evaporator to remove the mercury. The recovered mercury is then amalgamated, loaded out of the special enclosure, and sent to lag storage awaiting shipment to disposal. Lead-contaminated solids are handled in the same manner except, after shredding, they are placed in lag storage until ready to be encapsulated in polymer using the vibratory polymer process. Elemental mercury is amalgamated and placed in a disposal container and disposed of as is. Elemental lead (bricks and sheets) is repacked into baskets and loaded into a final disposal container and sent to the polymer encapsulation process for macroencapsulation in the vibratory polymer process.

Reactive metals will be deactivated by using a humidifier to oxidize the fines with humidified air and render them inactive. The fines will then be immobilized using the agitated grout process.

An offgas treatment system is provided for the mercury evaporation and amalgamation. The offgas is routed to a packed bed chemical scrubber and allowed to contact liquid to remove and neutralize chemical contaminates.

Liquid Waste Handling

It is the design and operational philosophy of WRAP Module 2A to be a zero liquid discharge facility and to solidify all liquid waste received and generated. WRAP Module 2A has the capability to collect liquid MLLW and liquid hazardous wastes generated from facility operations. Radioactively contaminated liquid wastes will be treated minimally and recycled for use in the treatment processes to the maximum extent possible. The nonradioactive contaminated liquid waste shall be collected separately from radioactive liquid for disposal.

The major treatment process consists of collection, sampling, pH adjustment of carbon absorption to remove organics, filtration to remove suspended/residual solids, and recycling back to the agitated grout process for

use in the grout process. If more liquid is collected than can be used in the grout process or excessive water from a plant upset (e.g., fire, facility decontamination) is used in the facility, loadout of the liquid to a truck fill area is provided as a backup capability.

Sample Management

The sample management area of WRAP Module 2A encompasses the following six major objectives:

- Incoming lot verification
- Characterization, as required
- Process control
- Certification
- Destructive examination
- Archive retrieval and storage.

As each lot of waste is defined, representative drums are brought into the sample management area where the waste will be sampled to confirm that treatment selection is correct for that lot of waste. This is commonly known as fingerprint sampling and can consist of anything from a visual inspection to a complete chemical analysis. Also, samples will be taken at various stages of processing to confirm that acceptable processing is occurring. Final waste form samples also will be taken to ensure that the final waste product meets disposal requirements.

Nondestructive Assay

WRAP Module 2A has the capability to assay containers of waste to determine the low-level waste category. As the drums are removed from the preconditioning area to the immobilization processes, they are routed through a nondestructive assay (NDA) area. The classification of the waste will be determined. The classification is based on the concentration of various radionuclides and the concentration limits are different for the various radionuclides. It was determined that classification before immobilization would provide the more accurate determination. This will provide an acceptable measurement of radionuclides within the tolerances limits established for certain radionuclides, which would be impossible to measure after the immobilization materials are added.

The equipment within the NDA area will consist of two passive-active neutron (PAN) instruments and two gamma energy analysis (GEA) units. The instruments need to be duplicated to achieve operational throughput requirements. The PAN system will determine transuranic (TRU) content because a potential exists that waste could contain TRU material (less than 100 nCi/g transuranic nuclide), and the GEA unit will measure the key gamma-emitting nuclide (^{137}Cs, ^{90}Sr, ^{90}Co), which is required to make the waste class designation. To ensure that the equipment will operate correctly, the units are placed in an isolated area of the facility and are surrounded by shielding to reduce the background to acceptable levels.

Support Services

WRAP Module 2A will have all the necessary support services (e.g., administrative areas, offices, control rooms, lunch rooms, change rooms, and storage areas necessary to facilitate WRAP Module 2A operations). Electrical systems, fire protection systems, potable water/sanitary waste systems, compressed air/inert gas/breathing air systems, process water/process chilled water systems, and ventilation systems will be provided as part of the design.

The design philosophy for the heating, ventilation, and air conditioning system in the process areas is to protect the outdoors from airborne contamination particulate generated by the waste handling and treatment

and also to provide safe and comfortable working conditions inside the facility. The objective is to ensure that the potential for worker exposure will be maintained as low as reasonably achievable by providing negative pressures betweens areas of low potential for airborne contaminations and areas of high potential for airborne contamination. Process enclosures will be provided in areas where the waste containers are open and the waste is unconfined. These enclosures will protect the facility from contamination spread and the workers from unnecessary exposure to the waste.

REFERENCES

1. Resource Conservation and Recovery Act of 1976, as amended, 42 USC 6901 et seq.
2. WAC 173-303, Dangerous Waste Regulations, Washington Administrative Code, as amended, Olympia, WA.
3. UE&C (United Engineers and Constructors), WRAP Module 2A Conceptual Design Report, UEC. Co., Englewood, CO (1992).

HAZARDOUS WASTE TREATMENT FACILITY AND SKID-MOUNTED TREATMENT SYSTEMS AT LOS ALAMOS

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ABSTRACT. To centralize treatment, storage, and staging areas for hazardous wastes, Los Alamos National Laboratory has designed a 1115 m^2 hazardous waste treatment facility. The facility will house a treatment room for each of four kinds of wastes: nonradioactive characteristic wastes, nonradioactive listed wastes, radioactive characteristic wastes, and radioactive listed wastes. The facility will be used for repacking labpacks, bulking small organic waste volumes, processing scintillation vials, treating reactives such as lithium hydride and pyrophoric uranium, treating contaminated solids such as barium sand, and treating plating wastes. The treated wastes will then be appropriately disposed of.

Separate treatment rooms will allow workers to avoid mixing waste types, prevent cross-contamination, and avoid or mitigate other hazards associated with treatment.

The ventilation air from the treatment areas may contain hazardous or radioactive dust. Gas may also leak from process equipment. The ventilation air will first be filtered before it is exhausted through the stack. After filtration, the exhaust air from each treatment room is fed to a common gas caustic scrubber on an outside pad. The treatment process includes separating solids and gases and neutralization or adsorption of the hazardous gases. There are two levels of exhaust in each treatment room, one for heavy gases and another for light gases.

Several features help mitigate or eliminate hazards associated with spills and releases: each treatment room is sealed and under slight negative pressure; each room has its own HEPA filtration; to avoid mixing of incompatible wastes and reagents, portable individual spill-containment trays are used for skids, each type of reagent, the sampling area, etc.; to limit the danger of spills, the waste is directly transferred from outside storage to the treatment room; to mitigate the consequences of a gas release in the room, mobile hoods are connected to the exhaust-air treatment system; the floor, walls, ceilings, fixtures, ducts, and piping are made of acid-resistant material or are coated; and several cleaning systems will minimize the amount of waste generated during cleanup.

Most processing equipment will be mounted on a skid dedicated to one waste type; the skid can then be moved in and out of a dedicated treatment area. The concept increases flexibility in treatment, because new skids can be built for new waste types. It also decreases the amount of floor space required because no idle equipment clutters the room.

INTRODUCTION

Los Alamos National Laboratory (LANL) is a multidisciplinary laboratory operated by the University of California for the Department of Energy. The principal mission of the Laboratory is designing and developing weapons for the nation's nuclear arsenal, but considerable research and development is directed toward the peaceful development of nuclear energy, including research on controlled nuclear reactions, fission reactions, nuclear safeguards, laser fusion, and medium-energy physics. This work is supported by basic research programs in physics, chemistry, earth sciences, metallurgy, mathematics, computer science,

and other disciplines. Additional programs are conducted in medicine, environment, and alternative energy.

Research activities are conducted at a variety of technical sites spread over 13,000 ha, and the Laboratory staff is about 10,000 employees. The variety of research activities creates an equally wide variety of waste streams. Because much of the work involves radioactive materials, the research activities generate mixed wastes, wastes that are both radioactive and hazardous under the Resource Conservation and Recovery Act (RCRA). Consistent with the activities of Laboratory, a wide variety of low-level mixed wastes are generated but in relatively small volumes.

Until 1986, low-level mixed wastes were handled as low-level radioactive wastes. Since 1986, low-level mixed wastes were put into storage, and plans were developed to treat these wastes. About 3000 drums of low-level mixed wastes have accumulated, and about 300 drums are added each year.

THE PROBLEM

A survey was conducted in 1989 to separate low-level mixed waste streams generated at LANL into treatability groups. Twenty-nine waste streams were identified based on chemical nature (Table I). The streams are separated into major streams, more than 100 drums in storage, and minor streams, less than 100 drums. These streams were then combined into about 17 treatability groups based on common approaches to chemical treatment. But data on the older wastes, or legacy wastes, was sketchy, and assumptions were made in separating the groups. As more characterization was completed, it became apparent that the same treatment process could not be applied to all the wastes grouped into a waste stream.

Table I. Low-level mixed waste groupings.

Major Waste Streams	Minor Waste Streams
wastewater treatment sludges	miscellaneous solvents
scintillation fluids and vials	halogenated
oil	nonhalogenated
liquids	in vermiculite
semisolids (grease and sludge)	miscellaneous ignitables
on vermiculite	trichloroacetic acid, ethanol, sodium phosphate
PCB-contaminated	solids contaminated as above
paint stripper, paint stripper trash, Chemstrip	oxidizers
nitrated rags	other solids
lithium hydride	miscellaneous corrosives
contaminated lead	acid, liquid
	acid, with EP toxic metals
	other/unknown
	miscellaneous reactives
	lithium, sodium, uranium, calcium
	cyanides
	other
	TC toxic metals
	labpacks
	organics
	unknown
	gas cylinders
	unknowns

For example, one waste stream is contaminated lead, most of which is in the form of lead bricks and shapes with surface contamination. It can be treated by decontamination and recycling back into the shielding pool. Also in the inventory are several drums of lead shot, several drums of soil with lead shot, and lead that has been activated by an accelerator. Clearly, the process selected for decontaminating most of the lead could not be applied to all the wastes.

Waste within a stream defined by chemical nature can be contaminated with different radionuclides. For example, scintillation vials can be contaminated with small concentrations (up to 10 nCi/L) of the radionuclides ^{3}H, ^{14}C, ^{32}P, and ^{131}I and with transuranic isotopes such as ^{238}Pu, ^{239}Pu, and ^{241}Am. Some lead pellets and bricks are known to be contaminated with transuranic isotopes while others are contaminated with fission products such as ^{60}Co, ^{90}Sr, and ^{137}Cs.

Given our knowledge of the waste at the time, defining all of the treatment processes needed was impossible. In addition, as a research facility, the nature of future waste changes as the research direction of the Laboratory changes. What was needed was a highly flexible approach aimed at treating relatively small volumes of mixed wastes.

THE SOLUTION

The solution to the problem is to build a facility that can accommodate a variety of treatment processes for both hazardous and mixed wastes. The building provides containment, utilities, and support functions for treatment. The treatment processes are skid mounted and portable. A treatment skid is placed in a treatment room and the waste treated in a campaign fashion. The treatment skid and other equipment are then decontaminated and stored, allowing the room to be used for a different treatment process.

Hazardous Waste Treatment Facility (HWTF)

The facility covers 1115 m^2 and includes four treatment rooms (Fig. 1-3). A hallway separates the building; radioactive and nonradioactive treatment rooms are on opposite sides of the hallway. The building includes central change rooms, an operations laboratory, maintenance and parts storage areas, and offices. Small tank farms adjacent to the building accumulate treated fluids and contain spills.

Several factors influence the design of the facility (Fig. 4):

- the need to avoid mixing waste types;
- waste hazard codes and the primary hazards of fire, explosion, corrosion, toxicity, and radioactivity;
- preventing cross contamination;
- preventing mixing incompatible wastes and reagents;
- minimizing the effects of corrosive fumes;
- reducing the possibility of acid and caustic leaks;
- treating process gases;
- mitigating the hazards of gas leaks;
- ensuring flexibility and maximum use of space;
- waste minimization; and
- controlling fugitive emissions.

To reduce risk, wastes will be accumulated for treatment in storage facilities separate from the HWTF.

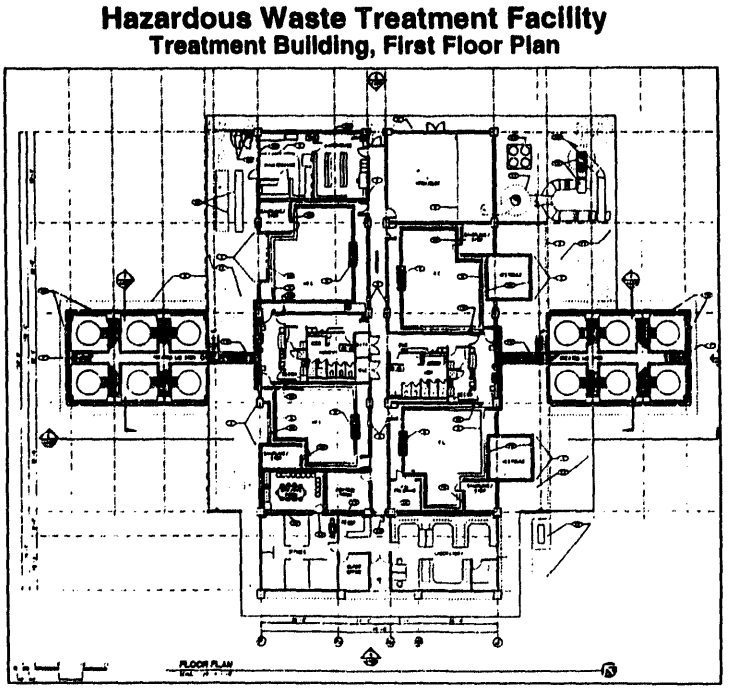

Figure 1. Treatment building, first floor plan.

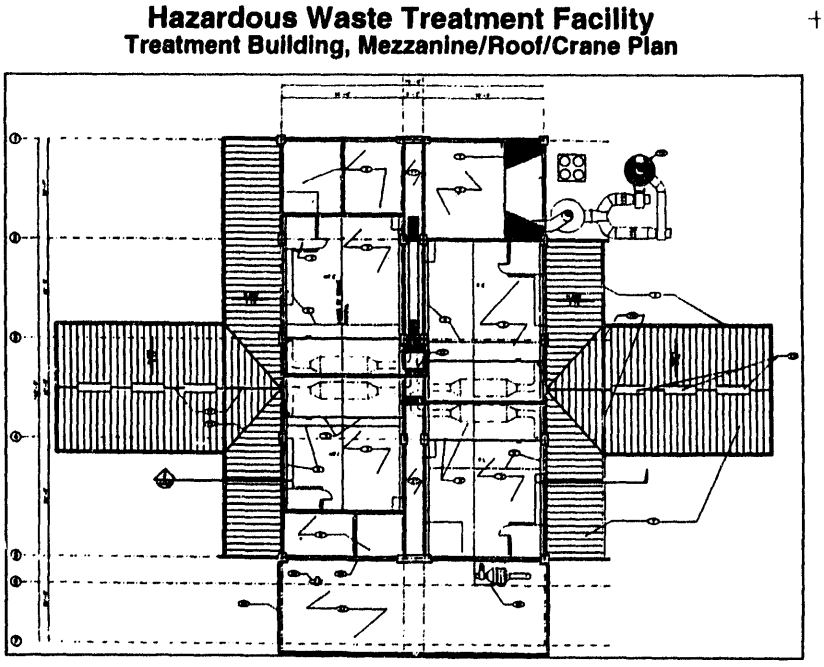

Figure 2. Treatment building, mezzanine/roof/crane plan.

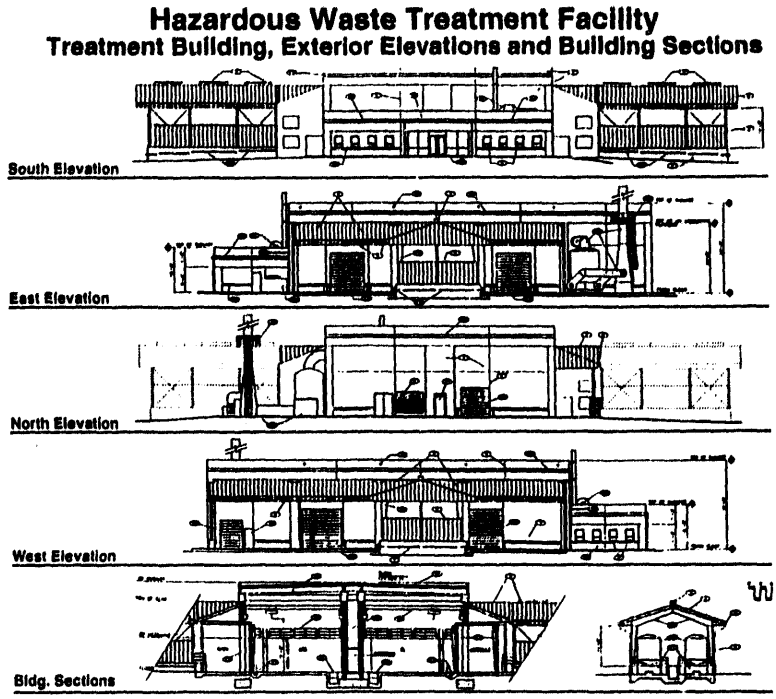

Figure 3. Treatment building, exterior elevations and building sections.

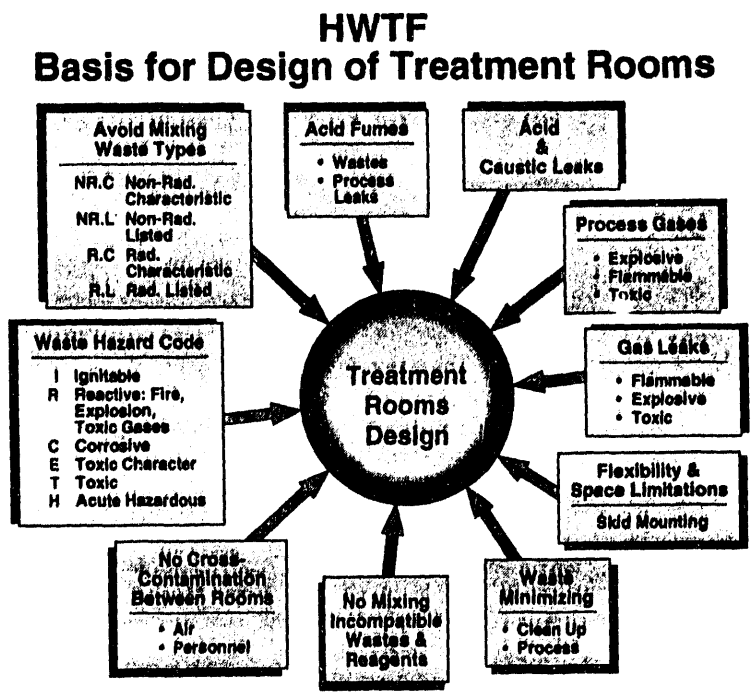

Figure 4. Basis for design of treatment rooms.

Treatment rooms. There are four treatment rooms, one room for each of the four kinds of waste: nonradioactive characteristic, nonradioactive listed, radioactive characteristic, and radioactive listed. Segregating the rooms reduces the risk of cross-contamination and simplifies treatment and disposal of residuals. The treatment rooms are nominally 110 m^2. Access to the rooms is through roll-up doors that allow the delivery of skids, wastes, and treatment reagents. Roll-up doors to rooms handling radioactive waste have air locks.

Treatment skids are delivered to the treatment rooms by forklifts or lowboy trailers. Inside the rooms an overhead crane positions the skids . Waste is moved with a variety of drum-handling equipment.

Air, water, steam, and electrical power are provided at stations at four locations in each room. Each room has a separate vacuum system.

Each treatment room has subroom for storing and sampling the waste associated with a treatment campaign. These small areas have special fire protection and ventilation hoods.

Ventilation. Individual skids include gas-treatment systems to handle off-gas and fumes generated in the treatment. The design of the off-gas treatment varies with the treatment process, but most off-gas treatment for mixed wastes includes a scrubber and high-efficiency particulate air (HEPA) filters.

Fixed or mobile fume hoods tied into the building exhaust system handle fugitive emissions from the skids.

The building exhaust system maintains the treatment rooms at negative pressure relative to the surrounding rooms and outside. The exhaust from each room passes through separate treatment units consisting of a prefilter, a first-stage HEPA filter, two charcoal absorption beds, and a second-stage HEPA filter.

The room exhaust is taken from the treatment rooms at both the ceiling and the floor to prevent the build up of gases that are lighter or heavier than air. The exhaust rate from the room provides seven air changes per hour when the building is "at rest" with no treatment in progress. Only two treatment rooms will be used at one time, so exhaust is borrowed from inactive rooms to support the exhaust needs in the active rooms. The exhaust control system will rebalance the system to treatment needs while maintaining all rooms under a negative pressure.

The combined exhaust from the rooms is treated with a caustic scrubber and passes through an exhaust fan to a stack. There are two exhaust fans, one in operation, the other a spare. An emergency generator ensures operation of the exhaust system during power failures.

Sampling and storage rooms have separate hoods in which to open and sample drummed waste.

Air and exhaust monitoring. The air in the treatment rooms is monitored for explosive and toxic gases. Rooms handling radioactive wastes are monitored for radiation. The building exhaust is continuously monitored for radioactivity, toxic gases, and hydrocarbons. The particulars of exhaust monitoring will be developed as part of the permitting process.

Secondary containment and spill control. Each treatment skid has drip pans to catch minor spills and leaks, thus keeping the treatment room clean during normal operations. The room floors are sealed and coated with a material resistant to acids and bases. The first four feet of the walls are coated with the same acid- and base-resistant material. The rest of the walls and the ceilings are sealed with an epoxy material.

The treatment room floors have interceptor trenches that drain to collection sumps. The sumps are equipped with explosion-proof pumps that transfer the liquid collected to one of three 9.4 m^3 tanks dedicated to that

room. Piping to the tank is contained in trenches or in double-walled pipes with leak detection.

Concrete basins provide secondary containment for the tanks. The floors of the basins slope to a collection sump with spill detection. A roof over the tank prevents accumulation of precipitation in the basins. Liquid collected in the sumps is pumped back with a portable pump to one of the three tanks or to treatment.

The tanks also hold fluids generated by treatment. These liquids are treated and discharged under permit or are solidified for disposal.

Wet and dry vacuum sweepers can be used to clean up small spills. The vacuum is provided by a vacuum pump in each room, with eight vacuum service points in each room.

Fire protection. The rooms are monitored for explosive gases, and all electrical service in the treatment rooms and on the treatment skids is explosion-proof.

Most of the building has a standard wet-pipe fire-protection sprinkler system. The four treatment rooms are protected by a high-expansion foam fire-suppression system. This system provides a foam with a low moisture content that is compatible with water-reactive wastes and reduces the amount of fluid generated by activation of the fire system. The sampling and storage areas have independent dry chemical systems using graphite or a similar powdered solid extinguishing agent.

The tank area is protected with a dry-pipe system.

TREATMENT SKIDS

The treatment process can be a single skid or multiple interconnected skids . A typical treatment process has three skids: one containing the reactor section, a second for gas handling, and a third for solids handling. As treatment designs progress, reuse of different skid components is expected. That is, the gas-handling and solids skids for one treatment process will apply to another.

The size of skids is dictated both by the need to conduct campaigns in a reasonable time and by the ability to move and site the skids in the treatment rooms. Mobility and siting set the maximum skid size at 1.5 m wide by 3 m long by 3.6 m high and a maximum weight of 2700 kg for each skid. Up to six skids could fit in a treatment room to make up a process.

Hazard and risk analysis are prepared for each treatment process concurrently; different design phases and engineered controls are incorporated in the design to minimize hazards and risks. Operating personnel are a major cost factor for waste treatment at LANL, so the selection of treatment processes emphasizes processes that can be operated for 8-hr days and left in a fail-safe mode overnight and on weekends.

The following processes are already in development.

Lead decontamination. The Laboratory will decontaminate lead by removing a thin superficial layer using an abrasive media of water, alumina, and air. This slurry version of sandblasting will be done at low pressure and will considerably reduce airborne lead particles and radioactivity. The slurry is recycled so the volume of effluent will be minimal, and it can be rendered nonhazardous by solidification.

When decontamination is completed, the lead will be washed with clean water. This water becomes contaminated with fine lead particulates. Most can be removed by settling and, when filtered through a 1.5 m filter, the residual lead concentration is about 0.01 mg/L. Approximately 200 L of this effluent will be produced per day. The decontamination process is in a semitrailer that includes a HEPA-filtered ventilation system. The process will begin operation in April 1993.

Uranium chips. When uranium metal is machined for defense applications, the process produces small chips and turnings, which are considered a waste that must be properly treated and disposed of.

As with some other metals, the smaller the pieces of uranium or the greater the surface area of the turnings, the more likely they will oxidize in the presence of air, water, or both. This oxidation process is exothermic and is accelerated by heat. Under certain conditions a mass of uranium chips could ignite spontaneously. If the mass of fine material is great enough, the reaction, once started, is self-sustaining, and temperatures can exceed 1000°C. Fine oxide particles can become airborne and would be hazardous if they were inhaled. If water is present, the reaction can produce hydrogen.

The treatment process at LANL allows low-temperature conversion of waste depleted uranium metal to uranium oxide. It avoids all the difficulties and hazards associated with high-temperature oxidation while using an environmentally benign oxidant, sodium hypochlorite, bleach, to oxidize the chips to produce an inert waste. Uranium turnings react rapidly with dilute solutions of sodium hypochlorite to form an insoluble uranium (VI) oxide as a finely divided bright yellow powder.

No soluble uranium products are formed. The oxidation is mild, occurs with dilute hypochlorite solutions, and is rapid. The resulting uranium oxide can be dissolved in dilute acids (pH 2 nitric acid) and readily separated from impurities, or reprocessed. The product oxide is suitable for either disposal after solidification, LANL's option, or, for ^{235}U, allows recycling back into the uranium process scheme and eliminating the oxide as a waste form. Oxide coatings (UO_2), formed when the reactive metal is exposed to air, do not deter the oxidation of the metal, and in fact are oxidized with the uranium as well.

Detailed design of the treatment skid is complete, and fabrication will start soon. Testing of the treatment process will start early in 1994.

Electroplating waste. Two or three drums of mixed plating wastes are produced every 2-3 years must be treated at the HWTF, and small volumes of mixed acids and bases must be neutralized.

The process follows the standard treatment procedure for plating wastes, providing oxidation of cyanides and ammonia and reduction of metals, which precipitate as metal sulfites and sulfides. Close control of pH is needed to prevent formation of hydrogen cyanide or hydrogen sulfide.

Final design of the skid is in progress.

Lithium hydride. Large quantities of lithium hydride and small quantities of reactive metals such as sodium and calcium are in storage. The recommended treatment for lithium hydride and other reactive metals is controlled oxidation with oxygen or water.

Reactivity of the water-reactive wastes is neutralized with an atmosphere of humid nitrogen, which prevents the formation of an explosive mixture of hydrogen and air. When the temperature of the nitrogen and the humidifier is adjusted, the nitrogen can be more or less humid, and the rate of reaction can be adjusted and controlled. LANL has investigated the rates of reaction of lithium hydride as a function of the temperature and humidity, and, as anticipated, they increase with increasing temperature and humidity.

Bench work is nearing completion and will lead to the start of a skid design.

DETOX process. Contaminated organic compounds can be treated using the DETOX process, an iron-catalyzed aqueous phase oxidation process.

The primary benefit of the process is the ability to catalytically oxidize organic constituents in a contained

reactor. DETOX is potentially more convenient to use than other forms of wet oxidation because it can accept a wide variety of waste streams and sizes; its lack of NO_x, SO_x, dioxin, or furan formation; its relatively low power usage; its containment and concentration of many heavy metals; and its ability to operate at moderate temperatures and near atmospheric conditions.

The transuranics and many other radionuclides would be contained and concentrated in the DETOX solution until their concentrations were sufficiently great to warrant recovery or disposal. Carbon-14 would be contained by absorption of carbon dioxide in sodium hydroxide to yield calcium carbonate. Tritium in the form of water would be contained in the reactor.

Results indicate that the DETOX process can destroy more than 99% of the organics, 99.94% for nonvolatile and >99.9999% for volatile. Future studies include operation of a continuous bench-top system.

Design of a treatment skid will start in 1994.

Barium sand. Thermal treatment of high-explosive (HE) scraps, HE-contaminated trash, and HE-contaminated equipment generates a sand waste containing soluble barium as barium oxide (a toxic waste), barium nitrate, and barium carbonate. If the toxic barium concentration exceeds the limits established by RCRA, the sand waste is a hazardous waste regulated under RCRA. Barium sand is not radioactive and is therefore not a mixed waste.

LANL treats the sand with hydrated calcium sulfate (gypsum) and sulfuric acid, which precipitate the barium as insoluble barium sulfate according to the reaction below and produce a sand with an EP toxic barium concentration below 100 mg/L.

$$BaO + H_2SO_4 \longrightarrow BaSO_4 + H_2O$$

Because the treated sand no longer shows any characteristic of a RCRA hazardous waste and is not a RCRA-listed waste, the sand is disposed of as a nonhazardous waste at a designated disposal area.

A customized "cement truck" can be backed into the treatment area, the sand and reagents loaded into the mixer drum from a portable process platform, and the treated waste mixed with cement and dumped into disposal shafts for in situ solidification. Personnel will not have to actually handle the waste.

The fabrication of a skid will begin as soon as permitting is completed.

Future Skids

The design of treatment processes for two wastes are started each year until there are enough processes to handle all waste streams. The waste streams are prioritized based on the risk of storage. Treatment processes for wastes with the highest storage risk are started first. The design of the treatment process is managed using a project management plan generic to all skids and addressing all the steps from waste characterization through skid testing.

Schedule. The conceptual Title I design for the HWTF has been completed. Allowing two years for permitting, completion of the facility is expected in 1998. Skids will be operated before the HWTF is completed at alternative sites as they are available and as permitting is completed. Lead decontamination will be operational in April 1993, and the uranium chips treatment is expected to be operational in 1994.

THE MIXED WASTE MANAGEMENT FACILITY AT THE LAWRENCE LIVERMORE NATIONAL LABORATORY

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ABSTRACT. The DOE has developed a National Mixed Waste Strategic Plan which calls for the construction of 2 to 9 mixed waste treatment centers in the Complex in the near future. LLNL is working to establish an integrated mixed waste technology development and demonstration system facility, the Mixed Waste Management Facility (MWMF), to support the U.S. Department of Energy (DOE) National Mixed Waste Strategic Plan. The MWMF will develop, demonstrate, test, and evaluate incinerator-alternatives which will comply with regulations governing the treatment and disposal of organic mixed wastes. LLNL will provide the DOE with engineering data for design and operation of new technologies which can be implemented in their mixed waste treatment centers.

MWMF will operate under real production plant conditions and process samples of real LLNL mixed waste. In addition to the destruction of organic mixed wastes, the development and demonstration will include waste feed preparation, material transport systems, aqueous treatment, off-gas treatment, and final forms, thus making it an integrated "cradle to grave" demonstration. Technologies from offsite as well as LLNL's will be tested and evaluated when they are ready for a pilot scale demonstration, according to the needs of the DOE.

INTRODUCTION

Under the sponsorship of the U.S. Department of Energy's (DOE) Office of Environmental Restoration and Waste Management, Lawrence Livermore National Laboratory (LLNL) is designing a facility for the demonstration of low-level mixed waste treatment. The Mixed Waste Management Facility's (MWMF) mission is to demonstrate technologies which are alternates to incineration for destroying organic constituents in mixed waste. This facility will support the DOE National Low-Level Mixed Waste Treatment Program (MWTP). It is an adjunct to another program at LLNL, the Decontamination and Waste Treatment Facility. It is intended to support the DOE in the development of a plan for the treatment and disposal of mixed waste. Engineering and permitting issues and cost and schedule performance information will be transmitted to the DOE MWTP for use in the deployment of full scale facilities elsewhere in the complex. The treatment technologies will be of modular design, thereby, enabling easy exchange of systems for testing and comparison. Therefore, this facility will be a flexible test bed for current and future technologies. An existing building at the Lawrence Livermore National Laboratory site, has been assigned for this mission. EM-30 has requested that this test bed capability be maintained for 10 to 20 years.

Balanced flow sheets are being developed to insure compatibility of scale between all the various operations and technologies. This is important since we are trying to demonstrate an integrated systems approach for treatment; that is to demonstrate handling and treatment from receiving the waste, characterization and sorting, waste preparation, treatment, secondary stream treatments, off gas treatment, final waste forms production, repackaging, and shipping. This systems approach will provide a complete picture of what is required to support a specific treatment technology. The facility will accept, integrate equipment and evaluate (technologies) of modular design from other DOE facilities and industry. By having an integrated facility, technologies may be compared side by side. The design will minimize worker exposure, secondary

waste generation and plant maintenance requirements.

FEED STREAMS

Five specific feed streams have been identified for treatment in the Mixed Waste Management Facility. These are:

Organic liquids-halogenated and nonhalogenated solvents, oils
Organic matrix solids-sludges, containing organics
Combustible debris
Predominately combustible
Lab packs-scintillation cocktails

Since the current mission of this facility is specifically to evaluate alternatives to incineration, other feed streams will be segregated as much as practical at the receiving and the feed preparation areas and will be returned for storage in the LLNL Hazardous Waste Management Facility.

Material Flow

The MWMF will consist of five functional areas. Receiving and Feed Preparation, Primary Treatment, Secondary Streams Treatment, Off-Gas Treatment, and Final Waste Forms Production (Fig. 1).

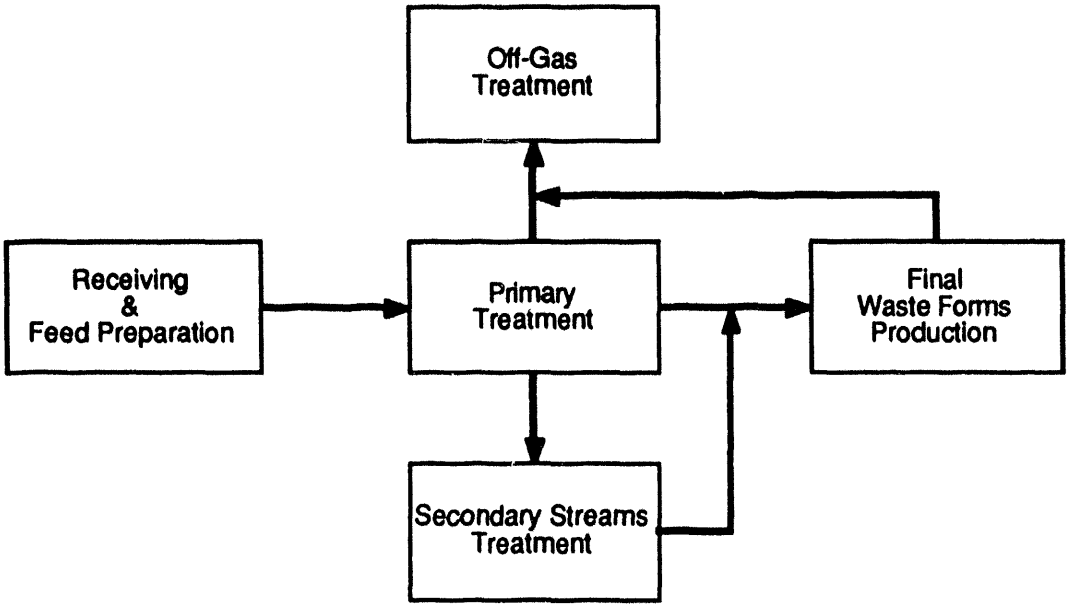
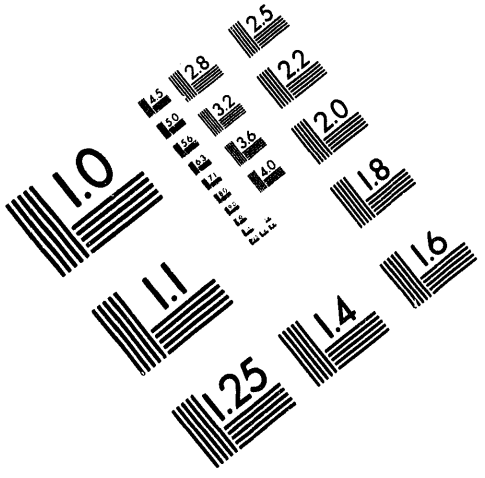


Figure 1. Mixed waste management facility functional block diagram.

Receiving and Feed Preparation

Waste materials will be received at the facility in a variety of containers. For initial operation, 55-gallon drums will be the largest containers accepted. However, provisions in design will be made to handle sizes up to and including DOT 7A (4'x4'x7') steel boxes (1). Prior to delivery to the facility, the smaller containers (55-gallon drums and smaller) will be examined by nondestructive means -- real time radiography, active-passive tomography, etc. Accepted containers will then be opened and unpacked. Initially, this task will be done with extensive operator involvement. As automated techniques evolve they will be integrated into the facility to reduce hands-on operation. The feed streams will be sorted into two categories -- liquids and solids (Fig. 2). The liquids will be analyzed, if required preprocessed by filtering



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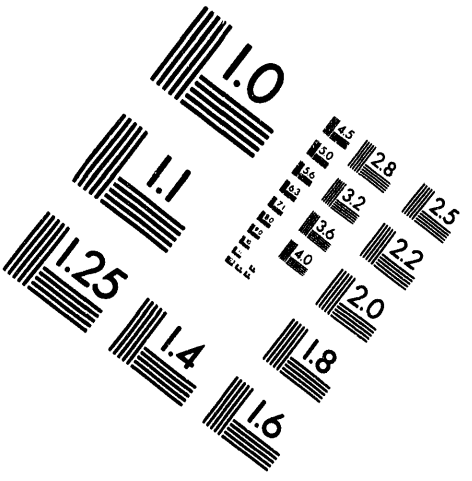

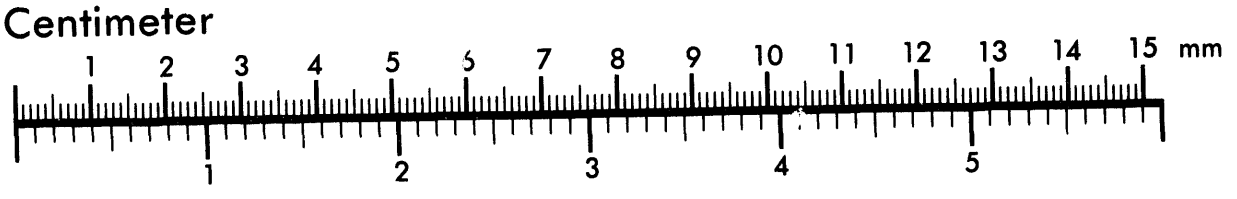

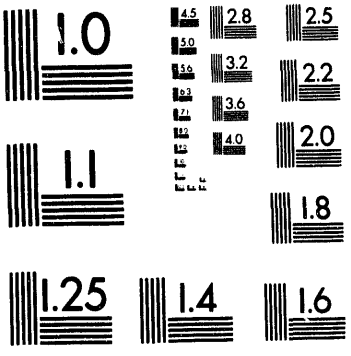

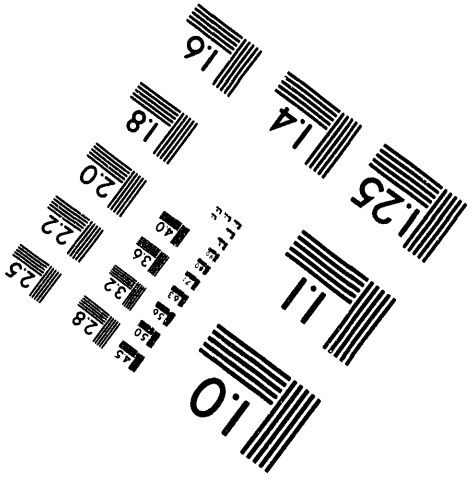

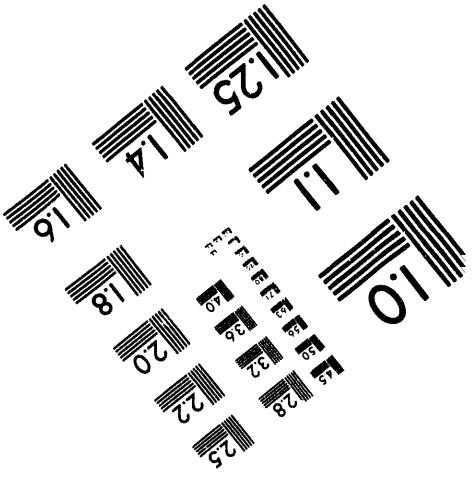

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to remove particulates, and stored according to type in queue to await treatment . The solids will be treated to remove the inorganic constituents, which will be returned for storage in the LLNL Hazardous Waste Management Facility. The combustible solids will then be pulverized and blended. In some cases, they will be mixed with liquids depending upon the treatment process to be used. They will be stored in queue to await treatment. Specific feed materials will be held until enough material has been accumulated for a one-week campaign using a specific technology. The material will be transported as required to the corresponding process technology for organic destruction. The transportation will be accomplished in a batch mode, and initially will be done manually. The intent is to upgrade this operation in the near future to be fully automated.

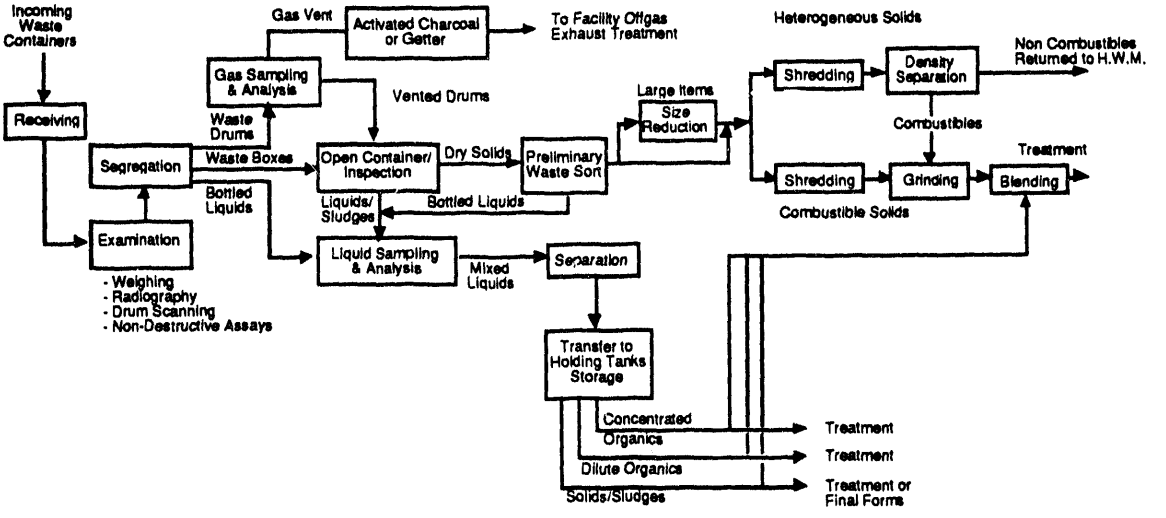

Figure 2. Receiving and feed preparation diagram.

Primary Treatment Technologies

Initially, four primary treatment technologies will be incorporated into the facility. These technologies will be modular, and will be complete with their unique supporting equipment (e.g., chemical regeneration, unique gas scrubbing equipment, power supplies, etc.). The initial technologies to be used are Molten Salt Destruction, Mediated Electrochemical Oxidation, Wet Oxidation, and Ultra-Violet Photolysis. These technologies are described in accompanying papers. Other technologies considered were super-critical water oxidation and direct chemical oxidation. At a later date, these technologies may be installed for testing.

Secondary Stream Processing

By far, the largest waste stream generated in the facility will be used process water. Water will be used in the sorting of organic from inorganic solids; it will be generated in the destruction of hydrocarbons and recovered from scrubbers. Water will be cleaned up and reused within the facility. Excess water will be further cleaned to meet discharge standards. Mediated electrochemical oxidization uses silver nitrate and nitric acid in its process. Silver recovery and reuse will avoid having to dispose of radioactively contaminated silver. Acid recovery will limit the inventory of acid required. Solvents used in the feed preparation area for rinsing organics from inorganic components and the rinsing of filters and strainers will be recycled, reused, or destroyed. Solid secondary streams are also accounted for. Carbonate salts from the molten salt process will be recovered and recycled. Non-metal filters and ion exchange resins will be sent through the solid feed preparation line and then will be treated to destroy the organic components.

Off-Gas Treatment

There are three component areas to the off-gas treatment -- the facility off-gas treatment, experimental off-gas treatment systems, and specific process equipment off-gas systems (Fig. 3). The facility off-gas system will use the Best Available Control Technology (BACT) described in the MWMF air permit. We anticipate this will consist of HEPA filtration, scrubbers, NO_X removal, and activated carbon filtration for volatile organic compounds. The experimental off-gas treatment is an area where new and emerging technologies may be demonstrated. These could include catalytic converters, advanced wet scrubbers, secondary oxidation, and metal HEPA filters. The specific process offgas treatment systems will be tailored to the requirements for each process (i.e., MSD, MEO, and WETOX).

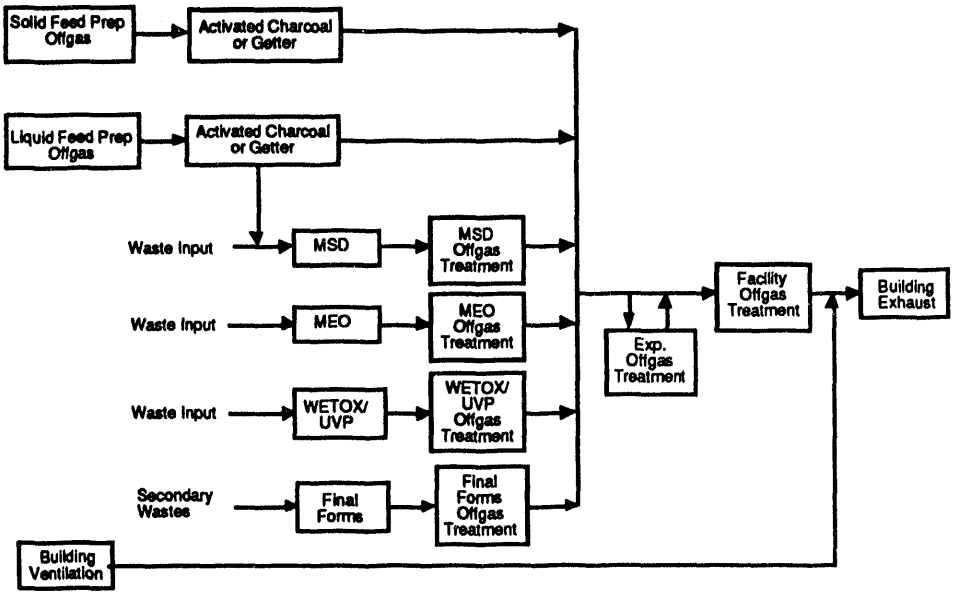

Figure 3. Off-gas treatment diagram.

Final Waste Forms Production

The primary final waste forms for the Mixed Waste Management Facility will be ceramics. Hydraulic cement will serve as a back-up waste form. The types of ceramics to be used are oxide, oxide-sulfide, and reaction-bonded phosphate. All will be made in the form of 1-cm sized pellets. The first two types will be produced by a cold press and 1200°C sinter process, while the phosphate type will be formed by phosphate bonding at room temperature followed by firing at 400°C. All final forms must pass the Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP) and the State of California's Waste Extraction Test.

PLANT CONTROL SYSTEM

The MWMF control system will consist of a central supervisory control room with operator consoles and computer servers networked to equipment in each of the functional areas as depicted in the data flow diagram in Fig. 4.

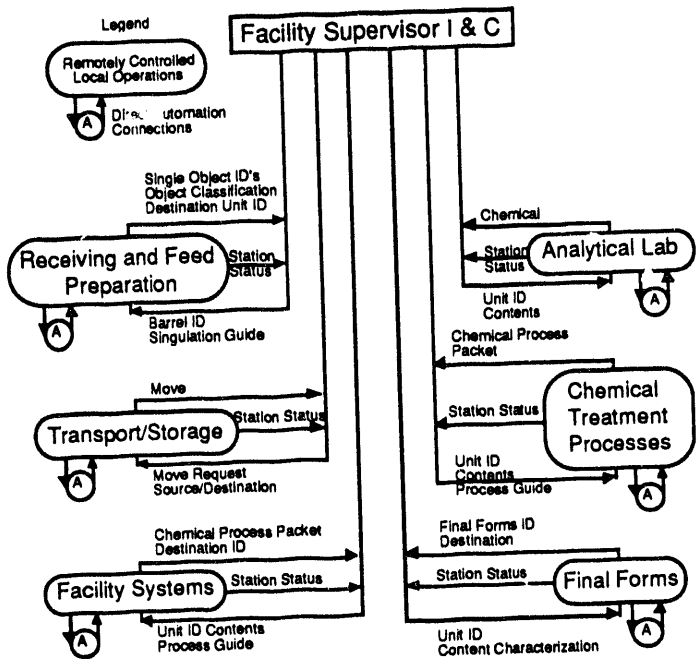

Figure 4. Plant control system diagram.

Each area will include monitoring, controlling, data gathering, remote view, and listening equipment. Communications will take place between central control and the functional areas over a distributed network.

The central control room will contain a control console at which the operator can monitor both global and local facility activities via computer graphics displays, an ensemble of TV monitors, and an intercom. The central control room will also include telerobotic consoles at which operators can teleoperationally control robots and other mechanisms in the various pre-treatment work cells.

The central control supervisor will also provide an assortment of data gathering, archiving, retrieving, managing, and trending services. Important functions which will use these services include tracking of waste materials movements from receiving, characterizing, feed preparation transporting, storing, processing, etc. Another important function of central control will be displaying the current conditions of all subsystems making up the facility including operational state, fire alarm status, etc. Waste characteristics and analytical results from processing will be managed within the central control system database.

Each process treatment area will be equipped with a local controller. This local controller will interface with the facility network as well as all local sensors (temperature, pressure, pH, flow rate, etc.) and all local effectors (heaters, coolers, valves, augers, etc.). The local controller includes a local operator console, and provides the PID and other controls necessary for running the process.

Environmental Safety and Health

The MWMF will meet all applicable ES&H requirements specified by Federal, State, and Local regulations as well as DOE orders. These include assessment of impacts under the National Environmental Policy Act and California Environmental Quality Act, permitting as a RD&D facility under the Resource Conservation and Recovery Act and California Hazardous Waste Control Law, air emissions controls and permits under the Clean Air Act and local air district requirements, as well as safety and health evaluations and operations under the Occupational Safety and Health Act and DOE orders. The successful completion of these tasks

will require establishing an effective working relationship between regulatory agencies (EPA, DTSC, DHS, and BAAQMD), DOE, LLNL, and the public.

CONCLUSION

Progress to date includes: preconceptual design, draft Environmental Assessment, draft Preliminary Analysis, acknowledgement from California that MWMF is eligible for an RD& D permit and a preliminary cost and schedule.

MWMF will provide the DOE with engineering data and operational experience for new alternative technologies. These technologies may be deployed nationwide as a part of the mixed waste treatment solution.

ACKNOWLEDGEMENT - Work performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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DESIGN CONSIDERATIONS FOR AN INTELLIGENT MOBILE ROBOT FOR MIXED-WASTE INSPECTION

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ABSTRACT. Large quantities of low-level radioactive waste are stored in steel drums at various U.S. Department of Energy (DOE) sites in the United States. Much of the stored waste qualifies as mixed waste and falls under U.S. Environmental Protection Agency regulations that require periodic inspection. A semi-autonomous mobile robot is being developed during Phase I of a DOE contract to perform the inspection task and consequently reduce the radiation exposure of inspection personnel. The nature of the inspection process, the resulting robot design requirements, and the current status of the project are the subjects of this paper.

INTRODUCTION

The objective of this paper is to determine what is required to design an automated inspection system based on (1) the specific wording of the federal regulations; (2) an examination of how a human inspector complies with the written regulations; and finally (3) how to translate the actions of a human inspector into equivalent actions of a semi-autonomous robotic system while considering the limitations of computer-controlled mechanisms and computer vision.

The reasons for automating a process currently accomplished using human senses is to

- Reduce the actual human exposure to ionizing radiation
- Minimize the potential human exposure to hazardous or toxic materials
- Match or improve the quality of the inspection process
- Minimize the manpower (and therefore cost) required for inspection.

The first step in the design process is to set down the requirements without regard to the limitations imposed by technology. The methods used to develop an actual system that complies with the design requirements is reserved for a future paper. This is a requirements document.

FEDERAL REGULATIONS

The general rules governing the storage of hazardous waste are spelled out in the Code of Federal Regulations (1). The rules that have specific implications regarding the inspection process may be summarized as follows:

- The owner or operator of a waste storage facility must inspect for malfunctions or deterioration that may cause or lead to a release to the environment or threaten human health (265.15).
- The owner operator must inspect often enough to identify and correct problems before harm is done (265.15).
- Records must be kept of the inspection process and must include a specified minimum amount of information (265.15).
- Notations regarding corrective action must be maintained (265.15).
- If a container is not in good condition or is leaking the contents must be transferred to good containers or manage the waste in some other way (265.171).
- Stored containers must be examined at least weekly to look for leaks and deterioration caused by corrosion or other factors (265.174).

The main reason for examining the federal regulations is that they contain a number of terms that are not defined in a scientific way and are open to subjective interpretation. These terms include

- malfunction
- deterioriation
- good condition
- corrosion
- leaks

It is likely that a human inspector would be able to conclude whether a drum or storage container is in "good condition". It is also likely that different inspectors would draw different conclusions based on the same drum when evaluating the degree of corrosion or deterioriation. Such variability is not acceptable when developing an automated system. An acceptable or non-acceptable degree of corrosion must be defined in order to develop a machine or computer-based vision system. Alternative sensors may be specified to substitute for the human senses of vision, touch and smell.

While an untrained inspector or a machine vision system may be able to conclude that a storage container is in "good condition", it is much more difficult to determine whether sufficient "deterioration" is present to require remedial action. This a very subjective determination and discussions with human inspectors has revealed a difference of opinion whether a specific storage drum should be repacked or not. Based on the difficulty of determining a degree of "poor condition", machine vision will be used to identify "suspect drums" with some degree of deterioration and leave the determination of "sufficient" deterioration to a human inspector. It is anticipated that separation of "good" from "suspect" will significantly reduce the work load of a human inspector.

Using current technology, machine vision algorithms are being developed to identify and inspect storage drums as well as visually assess the condition of the storage containers. Selected data will be maintained in a database suitable for meeting U.S. Environmental Protection Agency (EPA) reporting requirements.

In addition to removing inspectors from low-level radiation fields, automated inspection of storage sites has the potential of reducing the cost and improving the quality and efficiency of collecting data required to meet EPA inspection requirements.

INSPECTION OF MIXED WASTE

It is within technological feasibility to design a mobile robot to navigate up and down rows of stacked drums. It is a technical challenge to build a robot that can actually "inspect" the drums of waste. The

following scenario is proposed to analyze what a human would do during a walk-around inspection. The following tasks are proposed as the "inspection process":

Inventory Verification

Determine whether the drums present match the expected inventory of drums of stored waste in a warehouse. If the contents of a warehouse are actually known and has been documented in a database, such a database will serve as initialization data for future inspections. Otherwise, each container of stored waste must be inventoried by constructing a database that will serve as a starting inventory. The location of each item or drum is recorded and any change in inventory is recorded by adding or subtracting items from the data base. A non-automated inspection process may well maintain inventory records only by recording additions or deletions to the items in storage; however, an automated system would required identification of each drum. Barcoded and numbered labels are commonly used.

General Inspection

A human inspector would first form an opinion regarding the overall physical condition of each pallet and stack of drums. At an almost subconscious level, inspection would determine (a) whether the drums show any physical damage such as dents or gouges that could cause a problem at a later time; and (b) whether all the pallets are intact and undamaged. During future inspections the previous drum/pallet condition would be "recalled" to predict deteriorating conditions.

Close-up Inspection

A human inspector would make an immediate transition to a close-up inspection of any abnormal findings such as (a) dents, (b) serious scratches, (c) rust, or (d) evidence of leaking contents. Once again, a recall of the previous inspection would be required to determine whether abnormal findings indicated deteriorating conditions that could result in more serious leaks or drum failure. Without referring to previous inspection data a human inspector would make determinations regarding drum failure or serious leaks based simply on the overall and close-up appearance of the drum and the volume of leaking fluid as indicated by the appearance of streaks on the surface of the drum.

Leak Detection

Leaking drums are may be identified by fluid or dried streaks on the visible drum surfaces. Leaks could exist on hidden surfaces and these could only be detected if the leaks were of sufficient volume to stain the supporting pallets or floor. A reliable inspector would examine the streaks and determine whether they are getting worse and whether any of the leaking fluid has reached the floor. Condensation and rust on external drum surfaces can also produce streaks similar to leaks. These may be visually indistinguishable from streaks due to actual leaks.

Radiation Survey

Since low-level mixed waste has a radioactive component, a prudent inspector would monitor area gamma radiation for his own overall protection and would survey the floor for alpha and beta radiation to determine the contamination source substance.

Maintain Documentation

An inspection of a mixed-waste storage warehouse would ordinarily require some form of documentation indicating that an inspection had been performed on a certain date and either that no abnormalities were detected or that some abnormalities were detected and enumerated. Inventory would be validated by enumeration and the addition or subtraction of items shipped in or out. An actual drum count might not

be performed by a human inspector; however, an automated system would probably validate the inventory quantity by counting. Minimal records would only show date, inventory, and abnormal findings referenced to a numbered container while a more complete system would merely provide additional details on abnormal findings and any remedial action taken in response to visually detected drum damage. Detailed information about all the "normal" storage containers would not and should not be kept. An inventory item with a code or other indication that the drum had been inspected would be the sole record of normal drums or storage containers.

Corrective Action

EPA regulations indicate that an inspection has a purpose. Other than determining that all drum are present and accounted for, abnormal findings will lead, either to corrective action in the case of a serious leak or drum damage, or to further observation to detect deteriorating conditions that could become serious and require corrective action at a future time.

Meta-Inspection

EPA Regulation, 40 CFR 265.15 also requires that

> The owner or operator must develop and follow a written schedule for inspecting all monitoring equipment.... (1)

One might assume that an intelligent mobile inspection robot is considered "monitoring equipment" and therefore requires periodic inspection. Such an inspection of the inspection system would ordinarily be carried out automatically when the robot is "docked" and the batteries are being recharged. At this time the robot on-board control system would be directly coupled to the host computer system and an automated verification of the control electronics could be accomplished in addition to a visual inspection by operators. Since the robot navigation system will operate in a fail-safe mode, loss of supervisory control would cause the robot to halt in place. Back-up procedures would be used to retrieve the robot from the hazardous waste storage area.

The analysis just completed was designed to separate the human inspection process into a finite number of tasks that could be emulated by automated systems to the degree possible based on the limitations of technology. An automated mixed-waste inspection system could take alternative forms such as a wheeled mobile inspection robot with appropriate sensors and machine vision or a sensor package suspended from an existing over-head crane.

TECHNOLOGICAL CONSTRAINTS

Mobile Robot Inspectors

Mobile robots are commercially available that will navigate for hours along hallways or within warehouses while performing a "night watchman" type of task. At least one company (Cybermotion) has developed navigation algorithms that are sufficiently robust to make a robot night watchman economically justifiable. Approximately 50 systems are in use. Current efforts are underway to modify the hall-following algorithms to permit an autonomous system to navigate up and down rows of stacked drums of hazardous waste. While there may be some surprises in certain poorly structured facilities, mobile robot navigation is sufficiently well understood to be used for autonomous navigation in many hazardous-waste warehouses.

The Inspection Problem

The use of machine vision for autonomous drum inspection is at least as complicated as autonomous navigation and less progress has been made at the present time. If we restrict the robot inspection task to identifying drums that are not in "good condition", an autonomous system appears feasible. The precise wording of the Federal inspection regulations do not reject such a system since a human inspector will be used to validate the condition of a "suspect drum". An autonomous system that reduces the number of storage containers that must receive human inspection will greatly reduce human inspection time and exposure to hazardous environments.

The basis for most human inspection is vision, although touch and data acquired by other instrumentation can be used to supplement the visual images obtained by a person. A mobile inspection robot will be predominantly a vision-based machine with other subsystems dedicated to placing video cameras in locations appropriate for the visual scene acquisition. An intelligent inspection system will use computer-based artificial intelligence to make decisions during the inspection process rather than just allowing an operator to view a scene remotely or merely capturing a set of images for later analysis. Observing images of drums hour after hour by a human inspector is very tedious and would likely be ineffective once the inspector tired.

The alternative of simply collecting a set of images for later off-line analysis would also be less than optimum. Requirements of over 1 Mbyte of digitized data per image (uncompressed) would require enormous amounts of data to be collected, transported to a docking station, and transferred to an off-line computer. A 600 Mbyte compact disk (CD) could only store the images of approximately 600 drums whereas storage areas containing 3,000 to 5,000 drums are anticipated. The intelligent inspection robot described here performs on-line analysis of images and only retains digitized images of "suspect drums" that may be damaged or leaking.

Simple collection of digitized images using a lossy compression algorithm is also unsatisfactory. While regeneration of a visual display from a compressed stored image may be satisfactory when viewed by a human inspector, machine vision techniques are likely to suffer when evaluating images that have been compressed by a lossy algorithm. While the human visual system is able to "restore" missing information and ignore or overlook artifacts caused by compression, most machine vision systems are not able to perform a similar operation. However, some degree of compression is possible using one of several loss-less image data compression algorithms.

The overall inspection will be accomplished in two sequential phases. The first phase will acquire color images in the visual spectrum using the autonomous vision module. This module functions in real time while the mobile robot traverses rows of stacked drums containing mixed waste. During the second phase, follow-up inspection by a human in an operator-assisted mode would then employ additional robot dexterity to obtain close-up images, obtain drum-surface samples, or position other inspection instrumentation when it is desirable to remove the human inpector completely from the storage area.

Autonomous Visual Inspection

Current autonomous computer vision system capabilities are different from those of the human visual system. The goal of the Autonomous Vision Module is the real-time characterization of stored drums based upon passive visual information. This process spawns a number of challenging problems in image segmentation, feature extraction and classifier design.

The connotation 'real-time' is determined both by comparison with human inspection time requirements (nominally 1-2 sec/barrel for a cursory inspection) and the EPA frequency-of inspection requirements in relation to the total number of barrels to be inspected. The objective is to classify each barrel as either: (a)

"acceptable", i.e., the visual state of the barrel indicates no abnormal characteristics which warrant further investigation; or (b) "suspect", i.e., visual indications require human investigation for further assessment. Examples of the latter are the presence of significant rust streaks, deep rust, or significant bulging of the container. Thus, the overall visual inspection task becomes a c = 2-class classification problem.

Human scene analysis is guided by expectation (hypothesis verification) and iterative feature extraction (2). The visual and 3-dimensional structure of a typical "barrel" (e.g., DOT-17 55 gallon drums or other storage containers) or "barrels and pallet" is not too rich in structure relative to other possible man-made scene objects, particularly if the storage site is well organized. However, an initial autonomous system goal is determination that the current scene contains one or more barrels. This involves the process of image segmentation (2). Present segmentation algorithms use color, edge and regional textural information.

While one might be able to classify waste storage drums using a monochrome vision system, color images contain additional information that would aid in drum classification in spite of the additional system complexity. For example, in the human visual system, color provides important visual cues for segmentation and recognition. In addition, certain of the textural feature classes described below have a strong correlation with either specific colors or changes in color. To this end, the system converts input RGB images to HSI format for subsequent processing.

Once barrels have been identified, visual assessment of barrel condition is primarily an autonomous assessment of surface characteristics as depicted in the acquired image. This is a typical segmentation/classification problem (3). More importantly, specific classes of textural features must be identified, if present. Classes of textural features include:

- bar code labels
- rust or corrosion
- text (printed characters)
- icons (radiation symbols,etc.)
- leaks (typically with a strong vertical orientation); and
- good (textured region, but none of the above, e.g., barrel ridge)

Texture operators considered to date include:

- histogram and histogram-derived features
- directionally-oriented intensity variances
- co-occurrence matrices and derived features (e.g., contrast)
- entropy
- 2-dimensional moments and moment-derived features
- 2-dimensional Fourier spectrum and derived features.

Note that barcode label location is necessary for inventory. If the location and orientation of the barcode label varies significantly, the Autonomous vision module determines location and subsequently passes this location information to the barcode reader.

Fundamental to achieving the above objective is the acquisition of adequate and representative training data. In addition, the extraction of features requires determination of regions of interest (ROI). Using risk measures (as opposed to typical error minimization objective functions) allows a classifier design which is conservative, i.e., the classifier is designed to err more often by classifying an acceptable drum as suspect, rather than the converse. It is expected that this will yield far fewer drums for human inspection.

Illumination in a storage warehouse is likely to be inconsistent, at best. On-board lighting will be required. Strobe lighting, in contrast to continuous incandescent lighting, will be required to minimize stored energy requirements. Follow-up inspection by a human operator observing video images from a remote location may require continuous illumination.

In addition to conventional design of the textural and drum classifiers, the use of Artificial Neural Networks is being explored (4). Current results using monochrome textural features and small cardinality training sets (18 textures) are encouraging, and are to be extended with the integration of color feature information.

In summary, the objective of the autonomous vision module is to select "bad" or "suspect" images for subsequent human inspection. The system should err on the conservative side; i.e., it should label good drums as bad rather than miss a bad one. The autonomous vision module would be expected to store digital images of a relatively small number of "suspect" drums for human inspection (10-15%). Other information on drums in the warehouse inventory database ("acceptable" drums) will be stored in abstracted form; i.e., quantitative and qualitative results from the visual inspection.

Autonomous Robot Navigation

The basic purpose of the transport mechanism of a mobile robot inspection system is autonomously to move video cameras up and down rows of stored drums and locate specific storage drums with some degree of confidence that can be verified by video images and by scanning the bar-code label on a selected drum. Technically similar patrol robots are currently available commercially and are employed in warehouses, hospitals and offices complexes.

In order to function in the mixed-waste inspection role described above, a robot must be capable of autonomously navigating the rows of stored drums while performing automated visual inspection. Since storage drums are often stacked, it must be possible to position video cameras and other sensors to carry out the inspection process. When suspected leaks or other potential damage to the storage containers are discovered, the robot will assist in further investigation by relaying visual images to human operators and by providing dexterous manipulators suitable for examining or probing suspicious regions detected by the automated visual inspection. Based on the current sophistication of technology a mobile robot is able to carry out routine inspection with on-board autonomy but will require off-board assistance to accomplish more sophisticated tasks.

Mobile robots and schemes for autonomous navigation have been under investigation for a number of years at various universities and national laboratories. (5-8) Commercially available mobile robots are sufficiently agile to move in confined spaces. Ultrasonic sensors are used for navigation. The current navigation is based on "wall-following" or "hall-following" algorithms that may be enhanced for following rows of stacked drums. However, research has shown that autonomous navigation by robots currently available is not precise enough to permit the design of a machine that can navigate for extended periods of time without reference to known locations. Docking sites and beacons will be used for navigational reference locations, battery recharging, and for communication with off-board computers when needed for navigational updates or elaborate sensor integration algorithms.

Typical ultrasonic collision avoidance systems in current use consist of a control computer and an array of ultrasonic transducers. The system digitizes and stores the echo data returned from the environment. By applying digital signal processing techniques to this data, the ultrasonic system can detect objects as small as 1 in^2 in cross section over the entire volume in front of the vehicle and to a range of over six feet. Sophisticated ultrasonic systems provide a rich source of navigation information to the vehicle by extracting features from the echo data. Simple instructions allow this information to be used by the vehicle to correct its dead reckoning position estimate as it moves through a warehouse.

A typical commercial docking beacon system consists of vehicle mounted infra-red optical docking transponders and fixed-place docking beacons. The optical range is 12-16 ft. Each system consists of an optical head and a control assembly. An ultrasonic transducer allows the vehicle to dock a specified distance from the fixed station determined by an instruction argument. A vehicle is capable of docking at appropriate sites in the environment using a dock I.D. number in the docking instruction. At the docking locations dead reckoning estimates can be corrected. Once docked the vehicle can communicate at high speed with off-board systems.

System Control and Communication

A mobile inspection system will, of necessity, be a complicated distributed system under supervisory control of a base station and/or human operators. Primary tasks for off-board computing includes high-level planning and reasoning that cannot be done in the limited computing (due to space and power constraints) on-board. On-board computers will provide a dispatching function and on-board intelligence for local decisions and control. Simulation of operating environments can be cost effective and provide for efficient planning. Considerable research has gone into the design of such environments. A number of environments have been designed to control manipulators and robotic arms (9-13).

For each operator who works on a new robotic system, there is a learning curve. During the initial part of this curve, an operator is likely to make a number of mistakes. Even after an operator has become familiar with the system, any new ideas or software tried out on the system will be prone to errors or bugs. Each different environment (a new storage location, for example) presents new problems for the mobile robot. To minimize the ill-effects or accidents caused by improper handling during the initial stages or during the testing phases of software development it is especially convenient to have some tools available where these ideas can be exercised at a lesser risk.

Simulation has been a useful technique for analyzing and predicting a system's behavior. In the field of robotics, a number of systems have been developed which simulate robotic arms and manipulators. These systems have been used for designing robot work cells, analyzing the operation of manipulators, training personnel and suggesting improvements to existing robotic systems (14-17).

The robot control software consists of a collection of independent programs called tools or tasks (the terms tool and task are used interchangeably since a task is looked upon as being a tool in action). Each tool has a small but well-defined function and the user can have a number of tools executing concurrently. The execution of the tools, or more specifically their access to the robot, is governed by a single program called the User Interface, which does the scheduling. This approach to the design of the control environment is referred to as the toolkit approach. It follows closely the design philosophy of the UNIX operating system. The greatest advantage of this approach is its simplicity and extensibility. Each tool has a simple but well-defined function. More tools may be added without requiring code changes to the entire system.

Robot Manipulation and Dexterity

A completely autonomous mobile robot inspection system is probably not feasible using current technology. Human inspectors will be required to perform inspection tasks that are beyond the capability of passive computer-aided observation, however sophisticated. "Suspect Drums" will be identified at some point in the inspection process. and at this point a human operator must become involved.

At low-level waste sites a human inspector can enter the stoarage area and personally examine suspect drums identified by the robotic system. In storage areas with higher radiation levels, human entry will be undesirable and teleoperated or tele-managed manipulation and dexterity will be required for the human operator to provide a more detailed examination of suspect drums. A manipulator may be used to obtain close-up images, probe suspected corrosion, obtain samples of leaked material, and operate special sensors

used for alpha and beta radiation detection or ultra-sonic corrosion assessment.

A robot arm will be capable of utilizing different types of end effectors that may be required for inspection of waste containers or obtaining samples. For example, a camera attached on the end of a robot arm will allow inspection of areas that otherwise might be inaccessible if the camera is fixed to the mobile platform. By substituting various tools the arm can be used to probe, acquire samples, or otherwise investigate suspected leaks.

Since many of the tasks involving dexterity will require control of interaction forces as well as motion, the robot arm must have force-sensing capability. The tasks anticipated during storage drum inspection are highly unstructured and sensor-based information describing the environment must be incorporated into the low-level control algorithms (18). It is believed that the utilization of sensors (i.e. range detectors, vision systems, and end-effector force measurement devices) in the low-level control algorithm development will allow a robot manipulator to perform sophisticated tasks in unstructured environments.

It is expected that multiple sensor inputs will be incorporated into the low level control and task-level planning algorithms. The primary sub-areas in this area are force sensing and environmental "feature" detection. These two sensing capabilities are often required in many of the proposed robotic tasks. For example, during the probing of suspected leaks or container damage, the robot manipulator will come in contact with the environment; therefore, interaction forces develop between the robot manipulator and the environment. Consequently, these interaction forces, as well as the position of the end effector, must be measured and controlled.

Furthermore, it will be necessary to design and implement low-level control algorithms that are robust to unstructured environments and dynamic uncertainty introduced by manipulating unknown loads (19). The control algorithm must be capable of yielding high-performance for structured environmental tasks in the presence of uncertain actuator/manipulator dynamics, surface uncertainty, noise, and other disturbances before one can expect the addition of a vision system to yield high performance for unstructured environmental tasks in the presence of even more complex uncertainties. Some of the manipulator control features mentioned above are at the very edge of current robotics research.

Radiation Protection of Robot

Low-level radiation affects microcomputer circuitry. This is known theo-retically and from experience during prolonged satellite operation in radiation fields surrounding the earth. However, the radiation levels in the vacinity of low-level radioactive waste are not expected to cause permanent damage to computers and control electronics on the robot since defects introduced by ionizing radiation are "annealed" with the passage of time at normal room temperatures (20).

It is likely that commercial non-hardened microcomputers will function in somewhat higher radiation environments for some time before failure. However, without special testing designed to reveal low-dose-rate failure modes, the failure will be unpredictable since failure at low and moderate dose rates has been shown to differ from total-dose semiconductor failure at the high-dose rates typically used for Mil-Spec testing. In addition, commercial metal-oxide semiconductor devices may not behave predictably even when tested since the radiation-hardness is known to vary with manufacturing processes which may be altered from manufacturing lot-to-lot.

The levels of ionizing radiation near remote-handled transuranic hazardous waste could possibly cause cumulative damage to commercial-grade semiconductors and microcomputers. Radiation hardened semiconductors and microprocessors should be used to construct robot control systems if large cumulative doses of ionizing radiation are expected (21).

Since autonomous or semi-autonomous robot vehicles may fail while in a radiation environment, it is important to be able to either prevent radiation damage, predict the expected life, determine when failure is immanent, or find methods for eliminating defects caused by ionizing radiation. Radiation damage can be minimized by shielding or by storing a backup computer in a powered-down mode until needed. A total useful life in a radiation environment may be predictable if very expensive rad-hard devices are used that have very tightly controlled manufacturing processes. It may be possible to determine when failure is likely or immanent by monitoring leakage currents during exposure to ionizing radiation. Finally, it may be possible to reverse the effects of ionizing radiation (known as annealing) by removing a device from service and subjecting it to special procedures designed to remove any defects that have developed during operation.

Maintenance of Records

A intelligent mobile inspection robot would ordinarily obtain all data in digital form that could be stored in a computer data base and on archival backup media such as optical compact disks (CDs). Since each digital image of storage drums would occupy over 1 Mbyte of digital storage space, only digitized images showing abnormal findings would be placed in archival storage along with coded information regarding the condition of inspected storage containers.

A suggested inspection record for a storage container would include, the verified inventory number as bar-coded on the drum, a code indicating normal or abnormal condition, computer recorded date and time of the inspection, and a reference code identifying the supervisory inspector on duty when the automated inspection data was obtained. Pointers would reference a digitized image obtained the first time an abnormal finding was indicated by the inspection robot and any time the condition of the storage container changed significantly. Images would not be retained for normal-appearing drums or when images are unchanged with reference to a previously stored image. Pointers would also be used to reference records of any human inspection or corrective action that resulted from abnormal drum findings identified by the intelligent mobile inspection robot.

CONCLUSIONS

The operational requirements for an intelligent inspection robot have been examined in detail as a prerequisite to designing a prototype system. The process of inspecting stored mixed waste has been defined to the best of our ability in terms of the relevant Environmental Protection Agency regulations and the type of inspection that would be performed by a human inspector. Constraints imposed by the limitations of technology are identified that prevent a completly automated duplication of the human inspector. However, mobile robots can be programmed to carry out routine inspection tasks and report unusual findings and potential leaks for more detailed investigation by a person that could also be robot assisted.

Automated machine vision will be used during routine patrol of storage areas to detect potential problems with storage containers. The mobile robot will have both on-board and off-board computers to provide the necessary system intelligence. Machine vision algorithms are being developed to identify and inspect storage drums as well as visually assess the condition of the storage containers. Acquired data will be maintained in a database suitable for meeting EPA reporting requirements. A proposed minimum set of inspection requirements is shown in Table 1.

Table 1. Minimum Design Requirements for an Intelligent Mobile Inspection Robot.

1.	Possess adequate intelligence during an inspection task to operate autonomously while away from a fixed docking/charging station.
2.	Navigate in narrow aisles between stored drums.
3.	Reproduce position and orientation of video camera(s) within a work space extending from the floor to the top of drums stacked three high.
4.	Identify and determine physical location of bar-coded storage drums.
5.	Obtain video images of drums, and using computer vision techniques, discard the images of drums which are NOT damaged or show NO visual evidence of leaks.
6.	Relocate the transport at a designated location when required for close-up inspection.
7.	Provide for teleoperated visual inspection of drums by a remotely-located person when required.
8.	Permit operator-supervised manipulation of tools that may be needed to clean the bar-code label or perform other inspection tasks.
9.	If required, monitor floor alpha, beta, and gamma radiation to detect possible leaks or contamination that can not be observed visually.
10.	Maintain a data base of images and other inspection data that is required to meet EPA reporting requirements.

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CHAPTER 16

Environmental Restoration

MIXED WASTE IN ENVIRONMENTAL REMEDIATION

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ABSTRACT. This paper will describe specific environmental restoration activities underway or planned which have the potential to generate mixed waste. The paper will also discuss specific actions being taken to minimize the waste generated by these activities, and the treatment and disposal options being considered for managing the waste which is inevitably generated. This paper will also include an update on any recent regulatory issues which affect how the Environmental Restoration Program will manage its mixed waste.

BACKGROUND

The U.S. Department of Energy (DOE) operates a large industrial complex located at various production, processing, testing, and research and development installations across the country. For more than 40 years, the production of materials for nuclear weapons was DOE's top priority. The Office of Environmental Restoration and Waste Management (EM) was established in 1989, when DOE's top priority changed from nuclear weapons production to environmental cleanup. The Environmental Restoration (ER) Program within EM was tasked to perform this remediation and to ensure that risks to human health and the environment posed by DOE's past operations at its nuclear facilities and sites are eliminated or reduced to prescribed, safe levels. The EM Program is responsible for Waste Management, Environmental Restoration, and Technology Development activities at 134 locations in 34 states and one site in Puerto Rico.

DOE's restoration program covers a broad array of facilities and sites ranging from Florida, Texas, and California to Alaska, Michigan, and New York. The size of the remediation sites ranges from a few square feet to many square miles. Types of terrains range from flat sands, clays, and swamps to mesas, mountains, tundra, and high deserts. Buildings requiring remediation include individual structures with several acres under a single roof and buildings impregnated with explosives.

The DOE complex generated, and still continues to generate, significant quantities of radioactive, hazardous, and mixed waste, which the ER Program is now responsible for managing. Contaminants at ER sites and facilities include acids and bases, solvents, heavy metals, fuels, radioactivity, high explosives, and corrosives. The ER sites and facilities where these contaminants exist include nuclear reactors and laboratories, landfills, burial grounds, waste ponds, seepage pits/cribs, surface spills, buried debris, and ground water.

STATUS

ER's mixed waste program focuses on the transuranic (TRU) and low level mixed waste which will be generated as a result of environmental remediation. DOE's policy is to minimize the generation of new waste and, for existing waste, to use treatment, storage, and disposal technologies and facilities that comply with state and Federal regulations, as well as with internal DOE requirements.

Unfortunately, complying with applicable requirements for mixed waste in the ER program presents significant challenges. All necessary "how clean is clean" standards have not yet been developed. And most existing ER technologies are still low technology but relatively high cost such as dig up and move, or dig up, transport, treat, and re-dispose. DOE needs high technology solutions (such as in situ remediation) which would avoid exhumation, transportation, and re-disposal costs). Besides the cost savings which could be achieved through implementing higher technology solutions, DOE also believes these solutions are a more effective way to manage the waste.

ER's main responsibilities for mixed waste in environmental remediation include buildings awaiting decontamination and decommissioning, buried transuranic waste, and the tank hardware, residuals, and associated contamination plumes from underground storage tanks. In all cases, site and facility contaminants and plumes must be managed and a plan developed for long-term land use.

For buildings, DOE must evaluate whether re-use is feasible or if the buildings must be demolished. In cases where demolition will take place, DOE proposes to remove the top layers of contamination for appropriate disposal and recycle the remaining "clean" material. (More on this topic later.)

ER's responsibility for buried TRU-contaminated waste presents several challenges. For years, TRU waste was disposed of as low level waste in shallow, unlined land burial pits and trenches. Prior to 1970, the waste was stacked or dumped and frequently commingled with low level waste. In 1970, the Atomic Energy Commission issued guidance which established 10 nCi/g alpha contamination as a maximum suitable for routine shallow land burial. Because a practical technology to differentiate above or below 10 nCi/g did not exist at the time, sites began storing waste from facilities with the potential to generate TRU waste separately in 20-year retrievable storage. The 20-year retrievably-stored waste will be retrieved and assessed and that fraction greater than 100 nCi/g will be disposed of in an underground repository. However, the pre-1970 TRU-contaminated waste must be evaluated to determine appropriate long-term management.

Sampling results to date have been ambiguous, but it appears that some TRU and organic contaminants from this waste may be migrating to the subsurface and/or aquifer. Some buried TRU-contaminated waste may also potentially contain a mix of acids, bases, organics, and heavy metals, associated with the different types of materials which make up the waste (contaminated clothing, lab and glassware, failed equipment, etc.). This broad range of material coupled with the broad range of contaminants inhibit representative sampling.

The Hanford Site in Washington and the Idaho National Engineering Laboratory in Idaho have the largest volumes of pre-1970 TRU-contaminated waste. Pre-1970 disposed waste also exists at the Savannah River Site, the Oak Ridge Reservation, the Los Alamos National Laboratory, and a very small amount at the Sandia National Laboratory. For all pre-1970 buried TRU-contaminated waste, DOE is developing an update to the 1987 "Defense Waste Management Plan for Buried TRU-Contaminated Waste, TRU-Contaminated Soil, and Difficult-to-Certify TRU Waste," which will be available in late 1993. (An innovative approach to manage some of this waste is being pursued at the Idaho National Engineering Laboratory, as is discussed in a following paper.)

Underground storage tanks, such as the high level waste tanks at Hanford, also contain mixed waste contaminants. Currently, DOE's plan is to remove and treat these materials for disposal, at which point ER will become responsible for the remediation of the tanks and associated hardware, any residual materials, and any contamination plumes.

One of ER's greatest challenges is the management and minimization of waste generated from remediation. In situ treatment will be pursued where possible as the preferred remediation solution. With the application of new technologies, in situ treatment will be a better solution than digging up the

contaminants and moving them to another location for treatment, and possibly moving them again to a disposal site. In-situ remediation avoids the exhumation, transportation and storage, the associated risk to workers, the public, and the environment, and any secondary waste and its management.

Unfortunately, whether or not in situ remediation is pursued, it is very likely that not all sites and facilities can be cleaned up and made be available for unrestricted use. So even though the contamination will be immobilized and pose no environmental threat, some sites may still have restricted public access to reduce the risk to public health. In these cases, the Federal government will retain control of the sites. In other cases, where residual material left after the removal and transportation, treatment, and re-disposal of exhumed material may not allow unrestricted public access, specific uses (such as industrial activities) under controlled access could still be permitted.

The opportunity to recycle stands out as a bright light in DOE's efforts to manage mixed waste. Unfortunately, regulatory procedures for recycling are not currently in place. No release standards exist for large volumes of slightly contaminated materials. If DOE is unsuccessful in implementing recycling, both the environment and the economy will be insulted -- more damage is done to the environment by burying materials which may be reusable; plus, more damage is done to the environment and the economy by producing new materials to replace those just buried.

Mixed wastes, such as building rubble or contaminated metals, are ideal for recycling. For metals, the hazardous constituents (generally organics) will be destroyed during the melting/smelting process. Some contaminated metal recycling has been done in the US, and other countries are also recycling slightly contaminated metals such as aluminum. For rubble, the primary use would be as fill or road bases, in which the use itself would provide immobilization of the hazardous constituent.

CONCLUSION

DOE recognizes that the costs of the ER program cannot continue to escalate--the American taxpayers cannot afford it. However, DOE must continue to obtain funding adequate to address contaminants which pose a real risk to workers, the public, or the environment.

Working with the DOE waste management and the technology development programs, the ER Program will identify treatment, storage, and disposal methods that cost-effectively satisfy the regulatory and technical requirements for both the hazardous and radioactive components of the mixed waste which will be generated by remediation activities. In striking this balance, DOE will continue to work with the states, Indian tribes, the public, regulators, and other stakeholders, and demonstrate its ability to remediate sites and manage the resulting wastes in a safe and cost-effective manner.

MIXED DEBRIS TREATMENT AT THE IDAHO NATIONAL ENGINEERING LABORATORY (INEL)

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ABSTRACT. August 18, 1992 the Environmental Protection Agency (EPA) published the final revised treatment standards for hazardous debris, including mixed debris.(1) Whereas previous standards had been concentration based, the revised standards are performance based. Debris must be treated prior to land disposal, using specific technologies from one or more of the following families of debris treatment technologies: Extraction, destruction, or immobilization. Seventeen specific technologies with generic application are discussed in the final rule. The existing capabilities and types of debris at the INEL were evaluated against the debris rule to determine an overall treatment strategy for the INEL. Seven types of debris were identified: combustible, porous, non-porous, inherently hazardous, HEPA filters, asbestos contaminated, and reactive metals contaminated debris. With the exception of debris contaminated with reactive metals treatment can be achieved utilizing existing facilities coupled with minor modifications.

INTRODUCTION

Prior to the promulgation of the final rule for the treatment of hazardous debris,(1) debris destined for land disposal that was contaminated with a prohibited Resource Conservation and Recovery Act (RCRA) hazardous waste or that exhibited a prohibited RCRA hazardous characteristic was subject to the treatment standard for that listed waste or hazardous characteristic. However, debris is often a matrix significantly different from the underlying prohibited waste. Consequently the final rule, as an alternative, allows hazardous debris to be treated by specified technologies. Treatment is based on the type of debris and type of contaminant(s) present and is designed to remove contaminants contained on the debris. When treated with a specified technology that is an extraction or destruction technology the debris is no longer subject to RCRA regulation. This is particularly attractive in the case of mixed debris since debris thus treated could be disposed of at a low-level radioactive facility. Debris treated with an immobilization technology does not exit RCRA Subtitle C.

At the INEL a significant portion (~40%) of the current inventory of mixed low-level waste (MLLW) is debris. The five-year projection anticipates that 80% of the MLLW at the INEL will be debris.(2) Timely implementation of the debris treatment standards of the new rule would therefore provide much needed relief from Land Disposal Restrictions (LDR) affecting on-going work at the INEL.

OVERVIEW OF THE HAZARDOUS DEBRIS RULE

Hazardous debris is generally defined as solid material having a particle size of 60mm or larger and that is intended for land disposal and exhibits a characteristic of hazardous waste or that is contaminated with a listed hazardous waste. The definition includes mixtures of debris and other materials, such as soil, if the debris portion comprises the largest amount of material present by volume. Debris does not encompass waste for which a specific treatment standard has been established, such as radioactive lead solids.

The hazardous debris must be treated by one of the specified treatment technologies for each contaminant subject to treatment. Fortunately most of the specified technologies are generic in nature and therefore applicable to all contaminants. The choice of the technology is left up to the generator and/or the treater managing the waste. To ensure effective treatment, the treatment unit must meet certain performance standards or design and operating conditions.

Treatment Standards for Hazardous Debris

EPA has identified seventeen best demonstrated available technologies (BDATs) that it considers effective in substantially diminishing the toxicity of the waste or reducing the likelihood of migration of the waste's hazardous constituents. These technologies have been used at Superfund sites, to remove radioactive metals from debris, to treat debris-like material contaminated with compounds similar to hazardous constituents or, based on engineering judgement, are applicable to debris. Table 1 lists the seventeen treatment technologies under the three general categories of extraction, destruction or immobilization.

Table 1. Alternative Treatment Standards for Hazardous Debris

Extraction Technologies

Physical Extraction
- Abrasive blasting
- Scarification, grinding
- Spalling
- Vibratory finishing
- High pressure steam and water sprays

Chemical Extraction
- Water washing/spraying
- Liquid solvent extraction
- Vapor solvent extraction

Thermal Extraction
- High temperature metals recovery
- Thermal desorption

Destruction Technologies
- Biodegradation
- Chemical oxidation
- Chemical reduction
- Thermal destruction

Immobilization Technologies
- Macroencapsulation
- Microencapsulation
- Sealing

The EPA acknowledges in the rule(1) that it is particularly difficult to take representative samples of untreated debris. Therefore "the generator may presume that BDAT constituents for the listed waste are present at detectable levels and is not required to sample and analyze the debris to make that determination." The rule further states that "...enough contaminants subject to treatment will be identified for most debris to ensure effective treatment of other toxic contaminants that may be present." Consequently most of the debris treatment technologies specified in the rule are not restricted to specific contaminants other than metal vs. nonmetal.

The performance or design and operating requirements for each extraction and destruction technology were established to optimize treatment effectiveness such that hazardous contaminants would not be present at residual levels in the debris that could pose a hazard to human health and the environment. The obvious consequence of this approach is that the treated debris does not need to be sampled for the hazardous constituents. Once the performance standards or design and operating requirements are met the debris is no longer considered to be contaminated with the listed hazardous constituents. For example, physical extraction technologies such as high pressure steam and water sprays, when used to treat metal objects must remove foreign matter adhering to the metal to produce a "clean debris surface" as defined in the rule. A

technology such as abrasive blasting, when used to treat porous debris such as concrete must remove at least 0.6 cm of the surface and treat to the "clean debris surface". Extraction technologies remove the toxic constituents from the debris as treatment residues. These residues are subject to the LDRs for the waste contaminating the debris. Residuals from the destruction technologies, such as the ash from incineration, are also defined as treatment residuals and therefore are subject to the LDRs for the contaminants not destroyed by the destruction technology.

Unfortunately, the EPA was not able to develop objective performance or design and operating standards for all extraction and destruction technologies. Therefore the owner or operator of the treatment unit utilizing technologies without objective standards must make an "Equivalent Demonstration" to the EPA that documents that the technology treats contaminants such that the residual levels will not pose a hazard to human health and the environment absent hazardous waste control.

OFFICIAL INEL STRATEGY

On May 15, 1992, the EPA granted a generic case-by-case Land Disposal Restriction (LDR) Capacity Variance for certain hazardous debris .(3) The only exceptions are debris contaminated with listed solvent or dioxin waste and debris contaminated with non-liquid "California List Waste". To benefit from the Variance, individual facilities were required to document their strategy for managing and ultimately achieving treatment for their hazardous debris. Consequently the Idaho Chemical Processing Plant (ICPP), one of the facilities of the INEL, assembled the ICPP Mixed Debris Management Plan. It became obvious during the preparation of the management plan that the full treatment train for debris would not be in place until after the Variance expired on May 8, 1993.

The ICPP treatment strategy was refined to meet the final rule on hazardous debris and evolved into the official INEL strategy documented in the INEL application for extension of the debris case-by-case capacity variance in accordance with 40 CFR 268.5.(4) This application addressed all the types and quantities of debris expected to be generated by the INEL. The demonstrations required by 40 CFR 268.5 include efforts to locate treatment and disposal facilities, binding contractual commitments to construct or otherwise provide alternative treatment, recovery or disposal capacity, why alternative treatment cannot reasonably be made available by the applicable effective date, that sufficient capacity is being provided, a detailed schedule for obtaining alternative capacity, and adequacy capacity to manage waste during the period of the extension. The information summarized in the extension application provides the framework for the remainder of this paper.

The emphasis during the development of the strategy was to use existing facilities and existing technologies to the maximum extent possible. Additionally it was desirable to utilize technologies for which clear performance standards were delineated in the debris rule to minimize testing and subsequent submittals to the regulators under the "Equivalent Demonstration" clause of the treatment standards.

Treatment at Existing Facilities

Two existing facilities at the INEL can provide compliant treatment for six of the seven debris types being generated at the INEL. Minor or no modifications will be required at these facilities. Use of an existing off-site disposal facility will be necessary to complete treatment of two of the waste streams.

Non-porous Debris - High Pressure Steam and Water Washing. Non-porous debris such as metallic piping and components, glassware, plastics, rubber, etc. can be treated to a "clean debris surface" using standard decontamination techniques. The Decontamination Area within the New Waste Calcining Facility (NWCF) at the ICPP currently has the capability to perform this treatment. The NWCF is designed to convert highly radioactive acid solutions into a granular solid. Construction was completed in 1981 with service

commencing in August 1981. The facility, along with its associated tankage, storage of high-efficiency particulate air (HEPA) filters, and decontamination processes has RCRA interim status.

The Decontamination Area includes one level above grade and two levels below grade. The area contains equipment dedicated to the decontamination of tools and equipment from all parts of the ICPP. The above grade level includes the Low Level Decon Room, the Equipment Decon Room, and two decon cubicles. Equipment contaminated with higher levels of radioactive contamination are handled in the Filter Handling Cell, the Decon Cell, and the Equipment Decon Storage Area, all located in the second level (below grade). Used decon solutions are transferred to permitted storage tanks located on the third level of NWCF.

The capabilities within the Decontamination Area include high pressure steam and water washing in small sinks to a 25' X 30' spray booth for large components and equipment. Control of temperature, pressure, residence time, agitation (via ultrasonics), and the use of surfactants and detergents are part of the existing capabilities of the decon facilities. Using existing procedures, hazardous contaminants can be removed from debris surfaces.

Treatment is verified by Quality Assurance personnel using a special inspection procedure based on the "clean debris surface" criteria of the debris rule. "Clean debris surface" means the surface, when viewed without magnification, shall be free of all visible contaminated soil and hazardous waste except that residual staining from soil and waste consisting of light shadows, slight streaks, or minor discolorations, and soil and waste in cracks, crevices, and pits may be present provided that such staining and waste and soil in cracks, crevices, and pits shall be limited to no more than 5% of each square inch of surface area. The surface is evaluated against workmanship standards (i.e., photographs or standards showing acceptable surfaces). This is similar to the practice of evaluating blasted surfaces to the "near-white blast clean" criteria of the Steel Structures Painting Council.

The treatment capacity of the decon facility is about 200 cubic m^3/year. This is approximately equal to the annual non-porous debris generation rate at the INEL. The rinsate will be treated with other liquid mixed wastes at existing RCRA interim status facilities at the ICPP. A Part A Revision Justification for debris treatment and containment building storage for the NWCF has been submitted to the regulators. The treatment train consists of concentration via evaporation and conversion into a solid form via calcination. The calcine is stored in bin sets with a design life of 500 years. The final waste form will be a solid which meets the appropriate standards. All facilities except the high level waste vitrification facility are currently available and have interim status.

Porous Debris - Abrasive Blasting or Chemical Extraction. An assessment of the NWCF revealed that, with some modifications, the facility could be adapted to meet the performance standard (remove the top 0.6 cm of surface and achieve "clean debris surface") for physical extraction via abrasive blasting. A 1991 capital equipment request for carbon dioxide pellet blasting capabilities is scheduled for installation during FY94. A feasibility design study is currently underway to determine the options for the modifications necessary for the facility to be able to handle the solid residuals from abrasive blasting. Title Design and construction are scheduled for FY94.

Chemical extraction is an alternative treatment technology that is being examined for use with porous debris that is not amenable to abrasive blasting. However, this is a longer term effort since, in addition to any facility modifications, treatability studies would need to be conducted, "Equivalent Demonstration" petitions would need to be prepared, and approval obtained from the regulators.

HEPA Filters - Chemical Extraction via HEPA Leach System. The HEPA Filter Leaching System is used to leach hazardous and radioactive contaminants from HEPA filters. This system is located in the filter handling cell of NWCF and has RCRA interim status. After planned modifications, the facility will consist

of a leaching vessel, a drying vessel, and a handling table. After the filters are leached and rinsed, a filter basket containing the fibers will be disposed of as low-level radioactive waste and the leachate will be treated with other DOE liquid mixed waste at existing RCRA interim status facilities. Modifications to the NWCF to allow the HEPA filter leaching system to operate are scheduled for calendar year 1993 to support a startup during October 1993.

The regulators have requested that the data supporting an "Equivalency Demonstration" be submitted as part of the Waste Analysis Plan along with the Part B permit application. The current schedule has the submittal by midyear 1993.

Asbestos Contaminated with Mixed Constituents - Macroencapsulation. EPA has indicated that bagging asbestos in accordance with existing EPA and Occupational Safety and Health Act (OSHA) regulations meets the performance standards for macroencapsulation. Therefore such debris may be disposed of in a Subtitle C facility. The performance standard for macroencapsulation requires that the material be completely encapsulated and that the encapsulating material be resistent to degradation. The INEL triple bags asbestos contaminated with radioactive and hazardous constituents. This meets the OSHA and EPA standards. Asbestos debris is therefore "macroencapsulated" and will be sent to either Envirocare of Utah, Inc., for disposal in its Subtitle C facility, or a similarly permitted facility (no other facility has been identified to date for solid-phase mixed waste disposal).

At the time of writing this paper the disposal contract with Envirocare of Utah, Inc. is pending DOE approval of 1) the categorical exclusion under the National Environmental Policy Act (NEPA) and 2) an exemption to the DOE order that prohibits the use of commercial facilities for disposal of DOE radioactive waste.

Envirocare is permitted for low levels of radionuclides. As a result, some debris may require decontamination to meet the radionuclide limitations. Therefore the decontamination facility at the NWCF will need to be modified in order to accommodate decontamination of bulk asbestos. This is included in the current feasibility design study of the facility.

Combustible Debris - Incineration. Contaminated debris designated for incineration will be sent to the Waste Experimental Reduction Facility (WERF) incinerator located at the INEL. WERF is an existing facility which operates under RCRA interim status. It is a dual chamber, controlled air incinerator with an operating capacity of approximately 3100 m^3s/y. Achieved volume reductions are on the order of 300:1. Waste is fed dynamically at an average rate of about 181 kg/hr and the incinerator is generally operated in cycles of a feed/initial burn for 4 hours followed by a final burn for 4 hours. The flue gas cleanup and fly ash collection system consists of a baghouse and HEPA filtration. Typical feed for the WERF incinerator contains 50 wt% rags and paper, 35 wt% polyethylene, 10 wt% wood, and 5 wt% rubber.

Approximately 120 m^3/y of combustible mixed debris is generated at the INEL. The ash from WERF is stabilized with grout to meet the LDRs prior to disposal at a Subtitle C facility. WERF is scheduled to resume operations in 1993, pending the completion of maintenance activities.

An example of a combination of treatments is appropriate to discuss at this point. Depending upon the availability and costs associated with mixed waste disposal facilities vs. radioactive waste disposal facilities combustible debris could first be treated with a physical or chemical extraction technology to remove it from RCRA regulation. The debris could then be incinerated during a rad only run for volume reduction. The resultant ash would be disposed of at a rad only facility instead of a mixed waste disposal facility.

Inherently Hazardous Debris - Macroencapsulation followed by disposal at a Subtitle C facility. Inherently hazardous (IH) debris at the INEL refers generally to IH metals such as cadmium and silver solids

(radioactive lead solids are specifically excluded from the EPA definition of debris). If possible the IH debris, as well as radioactive lead solids, will be decontaminated and recycled, otherwise IH debris will be treated via an immobilization technology as required by the debris rule. In 1991 the INEL requested expansion under interim status to begin macroencapsulation at the Waste Reduction Operations Complex (WROC) with epoxy or vinyl ester resin coating as the expected treatment process. Assuming a favorable response on the requested modification to interim status, treatment with this unit is expected in 1994. Procurement of macroencapsulating equipment is in progress to perform generator treatment at the Test Reactor Area (TRA) for circuit boards generated by the Advanced Test Reactor (ATR). Treatment will be specified in a generator treatment plan and will be performed in FY93. As with all immobilization technology treatments the treatment must be followed by disposal at a Subtitle C facility. The previous discussion concerning Envirocare of Utah, Inc. is pertinent to the IH debris.

Treatment at Future Facilities

The seventh debris waste stream generated at the INEL will be treated at a proposed facility.

Reactive Metal Contaminated Debris - Deactivation/Chemical Extraction. Debris containing or contaminated with reactive metals (sodium and sodium-potassium) will be treated in the proposed Radioactive Sodium Waste Process Facility (RSWPF) at the Argonne National Laboratory-West (ANL-W). The RSWPF will provide capacity to remove and process sodium-potassium from radioactive materials and wastes produced or stored at ANL-W. As currently designed, the facility will process non TRU and TRU debris materials/waste.

Major features of the proposed facility will consist of an inert-atmosphere cell, hot repair area, truck dock, equipment access area, control room, operating corridor, and basement equipment areas. The facility will use existing ANL-W shielded radioactive material shipping casks, and will be interconnected to the existing radioactive liquid waste processing facility.

The current design method selected to remove and process reactive metals in the facility is the Melt-Drain-Evaporation-Calcination (MEDEC) process. This process initially removes reactive metals from components by heating and melting, evaporating any residual reactive metal under vacuum conditions, and converting the removed reactives to oxide form. This process has already been demonstrated at ANL-W using sodium. Due to the high cost of the RSWPF as it is currently designed (approximately $56M), funds have been allocated to revisit the design in calendar year 1993. Permitting efforts required for the facility will begin in 1994.

SUMMARY AND RECOMMENDATIONS

Due to the nature of the radioactive material handled at most DOE facilities, decontamination facilities similar to that at the NWCF exist throughout the DOE complex. Treatment of non-porous debris should be feasible with few if any modifications to existing capabilities and facilities. If liquid waste treatment facilities are not available at a particular location treatment to a "clean debris surface" can be achieved on most non-porous debris via CO_2 pellet blasting, which does not generate any secondary liquid waste. The contaminants which are effectively separated from the debris without generating a secondary waste can then be stabilized to meet the LDRs and disposed of at a Subtitle C facility. Meeting the containment building requirements for non-liquid debris treatment requires nothing more than a building with walls, a roof, and a method for controlling fugitive emissions.

For DOE sites that do not have permitted mixed waste incinerators capable of handling combustible debris, DOE should consider using excess capacity at incinerators such as WERF before funding is approved for additional incinerators. The significant additional costs associated with obtaining permits for new

incinerators would be avoided with this type of approach. This approach will result in lower costs/kg and more efficient operation at existing incinerators.

For mixed debris that requires an immobilization technology such as macroencapsulation, DOE is pursuing a complex-wide contract with Envirocare of Utah, Inc. as well as a blanket exemption from the DOE order prohibiting disposal of DOE radioactive waste at a commercial facility. NEPA requirements will need to be met by each site and is best handled as part of the project or activity that generates the debris. Section 1021.410 (d) of the DOE NEPA implementing procedures(5) states that "A class of actions includes activities foreseeably necessary to proposals encompassed with in the class of actions (such as transportation activities and award of implementing grants and contracts)".

With the exception of debris contaminated with reactive metals most other types of debris can be treated using existing technologies and existing facilities. Complex treatments such as mixed waste incinerators and reactive metal treatment processes should be coordinated on a complex-wide basis to ensure cost effectiveness and maximum efficiency.

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PIT 9 PROJECT: A PRIVATE SECTOR INITIATIVE

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ABSTRACT. The Pit 9 Comprehensive Demonstration is intended to demonstrate a cost-effective approach to remediate an Idaho National Engineering Laboratory (INEL) waste disposal pit through a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Interim Action. The remediation will include additional requirements, if needed, to provide high confidence that only minor additional work would be necessary to accomplish the final closure as part of the overall final closure strategy for the INEL's Subsurface Disposal Area (SDA).

Pit 9 is an inactive waste disposal pit located in the northeastern corner of the SDA at the INEL's Radioactive Waste Management Complex (RWMC). It covers approximately 1 acre. The waste within Pit 9 is primarily transuranic waste generated at the Rocky Flats Plant and additional wastes, both hazardous and low-level radioactive, from generators at the INEL.

The project mission is to remove, treat and dispose of all wastes in Pit 9 identified as risk drivers at a minimum cost to U.S. Department of Energy (DOE) using a private sector, turnkey, "grave-to-grave" solution while complying with all laws and regulations. The overall project objective is to find a "faster, better, cheaper" approach to cleanup at a DOE waste site. Other objectives include the establishment of a transuranic/radionuclide cleanup level and determining actual private sector capabilities.

Technical, financial and contractual information and lessons learned from the Pit 9 project will be factored into the planning for remediation of other DOE waste sites and be used to determine the feasibility of obtaining private sector participation in DOE/M&O environmental restoration activities.

INTRODUCTION

The Pit 9 Comprehensive Demonstration Project is a U.S. Department of Energy (DOE) initiative and pilot project supporting remediation of the Idaho National Engineering Laboratory (INEL) Radioactive Waste Management Complex (RWMC) Subsurface Disposal Area (SDA) and obtaining private sector participation in DOE Environmental Restoration Programs. The project would be the first large-scale remediation of a transuranic (TRU) contaminated hazardous waste burial site.

The purpose of the Pit 9 cleanup is to expedite the overall cleanup at the RWMC and to reduce the risks associated with the potential migration of Pit 9 wastes to the Snake River Plain Aquifer. The project will achieve the following technical goals:

- Effect a near-term remediation of plutonium, americium, and identified risk drivers (hazardous waste) in Pit 9 at a minimum cost to DOE such that minimal or no future remediation is required
- Eliminate Pit 9 as a potential source of environmental contamination thereby protecting human health and the environment from possible future exposure to contaminants located within Pit 9
- Demonstrate private industry's capabilities for remediating transuranic-contaminated mixed waste sites

In accordance with the INEL Federal Facility Agreement and Consent Order (FFA/CO) between the Idaho Department of Health and Welfare, the U.S. Environmental Protection Agency, and the DOE, activities at Pit 9 would be conducted within interim action guidelines under the 40 Code of Federal Regulations Part 300 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (1). After screening the existing remedial technologies that could be used to clean up a mixed waste site such as Pit 9, the Agencies determined that the preferred alternative for cleanup of Pit 9 is a combination of physical separation, chemical extraction, and stabilization technologies.

SITE BACKGROUND

Pit 9 is located in the northeast corner of the SDA at the RWMC. Waste was placed in Pit 9 from November 1967 to June 1969. It presently has an overburden that averages about 1.8 meters thick. There was approximately 7,000 m^3 of overburden, 4,200 m^3 of packaged waste, and 9,800 m^3 of soil between and below the buried waste at the time of Pit 9 closure. The depth of the pit from ground surface to bedrock is approximately 5 m and the horizontal dimensions are approximately 39 by 116 m.

The inventory of wastes buried in Pit 9 was estimated from available shipping records and the Radioactive Waste Management Information System (RWMIS). The waste in Pit 9 is primarily transuranic (TRU) waste generated at the Rocky Flats Plant and additional wastes (primarily low-level waste) from waste generators at the INEL. Approximately 3,080 m^3 of waste buried in Pit 9 was generated at the Rocky Flats Plant, and consisted of drums of sludge (contaminated with a mixture of transuranic and organic solvents), drums of assorted solid waste, and cardboard boxes containing empty contaminated drums. Approximately 4,000 drums; 2,500 boxes (approximately 1,500 contained empty contaminated drums); and 80 unspecified containers of waste were buried in Pit 9. In general, the boxes were disposed at the north end of the pit and the drums were dumped in the south end, although intermixing of containers in the pit did occur due to flooding in 1969.

REGULATORY BACKGROUND

In addition to the preferred alternative, four remedial alternatives were presented for public review and comment in the Revised Proposed Plan for a Cleanup of Pit 9 at the RWMC, INEL: No Action, In-Situ Vitrification, Ex-Situ Vitrification, and Complete Removal, Storage, and Off-Site Disposal (2). The proposed use of chemical extraction/physical separation/stabilization technologies for Pit 9 remediation was generally supported by the public, and a draft Record of Decision (ROD) is scheduled for regulatory approval in May 1993 (3).

In accordance with the DOE orders, the National Environmental Policy Act (NEPA) and CERCLA processes are being integrated for the project. The CERCLA proposed plan for the Pit 9 interim action incorporated appropriate NEPA values and served, in conjunction with a supplementary document, as the environmental assessment.

Pit 9 was designated Operable Unit (OU) 7-10 in Waste Area Group (WAG) 7 in the INEL FFA/CO. The

Pit 9 interim action is intended to reduce the risks associated with waste materials within Pit 9 only. Contaminants in the vadose zone and their effect on the Snake River Plain Aquifer in the vicinity of the SDA will be evaluated in the OU 7-08 Remedial Investigation/Feasibility Study (RI/FS), and remedial action will be undertaken as necessary. A complete evaluation of all risks associated with CERCLA actions for all TRU contaminated pits and trenches, including a re-evaluation of Pit 9, will be conducted as part of the TRU-Contaminated Pits and Trenches OU 7-13, RI/FS. A complete evaluation of all risks associated with CERCLA actions at WAG 7 will be conducted as part of the final comprehensive OU 7-14 RI/FS.

The regulatory approach in the draft ROD supports a near term remediation of major risk drivers in the pit such that minimal or no future remediation is required. Where proof-of-process and limited production testing do not achieve cleanup or cost effectiveness goals, Pit 9 contamination will be addressed in an amendment to the ROD or in the RI/FS for the TRU Contaminated Pits and Trenches (OU 7-13).

PROJECT DESCRIPTION

Procurement History

Over the last several years, private industry has been lobbying the DOE to include them in environmental restoration activities. They cited readily available technology which could be used to rapidly remediate hazardous mixed-waste sites. In response, DOE took the initiative to establish the cleanup of Pit 9 as an innovative project, with one of the goals to include private industry participation.

EG&G Idaho, Inc. is tasked by DOE with coordinating the remediation of Pit 9. The strategy developed and implemented to carry out that remediation involves a three-phase project. The phases: (1) Proof-of-Process (POP) test, (2) Limited Production Test (LPT), and (3) full-scale remediation, are designed to allow demonstration of proposed technologies and correction of problems in controlled environments such that remediation is done in a safe, cost-effective, and rapid manner.

With that precept as the foundation of the project, Request for Proposal (RFP) No. C91-133136 was issued November 19, 1991, to qualified respondents to the Commerce Business Daily (CBD) advertisements of March 14, 1991; March 28, 1991; May 2, 1991; and any other prospective firms as a result of a procurement survey (4). Three teams responded to the RFP and submitted technical proposals on January 20, 1992. A Source Evaluation Board (SEB) consisting of technical experts throughout EG&G Idaho reviewed each proposal for the next six weeks and evaluated their technical adequacy based on criteria contained in the RFP. Technical clarifications with each team were also conducted on location. At the end of February, the SEB concluded that the Waste Management Environmental Services (WMES) and Lockheed Corporation proposals were essentially equivalent but technical questions needed to be addressed (5,6). The third team was dropped from further consideration. A request for discussion of technical issues was sent in March, and responses received in April 1992. The SEB evaluated the revised proposals and concluded again that both the WMES and Lockheed proposed processes were technically equal, but with reservations associated with the degree of technological development and process integration. The decision was made to revise the project strategy and have both teams conduct an expanded POP test, at the conclusion of which one team would be selected to continue the project as originally planned.

The expanded POP scope was explained to both subcontractors and upon acceptance extensive negotiations conducted. During negotiations, a detailed Scope of Work (SOW) was developed, terms and conditions agreed to, and a schedule for project deliverables finalized. The agreements reached were formalized into letter subcontracts executed by EG&G Idaho on November 12, 1992, specifying a SOW that could be performed under an $8 million, fixed-price, lump-sum, pay-for-performance, one year contract (7).

Project Strategy

The individual processes for this action are proven technologies, but the integration of the process systems has not been demonstrated on waste forms such as those found in Pit 9. The test phases will be performed within the interim action for Pit 9 before full-scale remediation to confirm that treatment standards can be met and to identify the most cost effective technique or combination of techniques for use in the remedial design. Both test phases must be successfully completed before full-scale remediation. Decontaminating and demobilizing the facility is part of the proposed action.

The proof-of-process tests will demonstrate critical aspects of the preferred alternative and prove that the integrated processes to be used are effective in achieving cleanup goals. The POP tests include design, fabrication, and operation of pilot scale and demonstration equipment and systems, and laboratory analyses. Surrogates of plutonium and americium will be used for the tests which will be conducted at subcontractor facilities not located on the INEL site.

The major phases of the WMES POP test program include the following:

- Radiological instrumentation demonstration performed at Pajarito Scientific Corporation facility in Los Alamos, New Mexico
- Off-site laboratory demonstration performed at the WMES Clemson Technical Center (CTC) in Clemson, South Carolina
- Treatment process demonstration performed at the CTC
- Product waste form demonstration performed at CTC.

The key element of the WMES POP, the treatment process demonstration, will demonstrate the ability of the chemical separation process(es) to perform as an integrated system at pilot or engineering scale for a minimum of 100 hours on a schedule that would be used for actual remediation.

The Lockheed POP test program includes:

- Soil processing and off-site laboratory demonstration performed at Lockheed's remediation testing laboratory in Las Vegas, Nevada
- Plasma waste processing demonstration performed at the Component Development and Integration Facility in Butte, Montana
- Plasma melter remote maintenance demonstration at Ukiah, California
- Instrumentation demonstration performed at the Pajarito Scientific Corporation facility in Los Alamos, New Mexico.

The key element of the Lockheed POP, the plasma waste processing demonstration, must demonstrate the ability of the thermal stabilization system and off-gas exhaust system to operate for a minimum of 100 hours on a schedule that would be used for actual remediation at a minimum feed rate of 136 to 227 kg/hr.

The limited production test is intended to demonstrate that all integrated systems will function as proposed and demonstrate reliability of the systems before starting full-scale remediation. The limited production test will involve the same processes, area, and impacts as the remediation phase but on a smaller scale. Surrogates of plutonium and americium would be used initially in the test before materials from Pit 9 are processed through the system.

The final phase will be full-scale remediation after successfully completing the limited production tests. Under the criteria for residuals returned to Pit 9, or for waste left in place in the pit, the concentration of

contaminants will be reduced based on an industrial risk scenario of 1 in 10,000 for carcinogenic risk or <1 hazard index for noncarcinogenic health effects. To attain the performance goal, the treatment standards for contaminants in Pit 9 are:

1. Average concentrations of transuranic isotopes in residuals (i.e., treated waste streams) being returned to Pit 9 would be <10 nanocuries per gram (nCi/g)
2. Wastes and/or materials in Pit 9 containing >10 nCi/g transuranics will be treated to reduce the volume by >90% (in addition to meeting the treatment standard in 1 above) before being returned to the pit
3. For materials being treated and returned to Pit 9, all Applicable or Relevant and Appropriate Requirements (including land disposal restrictions) will be met.

During full-scale remediation an estimated 14,000 m^3 of soil and other materials contaminated with hazardous materials and TRU wastes would be excavated from the pit. The entire pit would be excavated, with materials being segregated for treatment at the dig face by using radiation monitoring equipment for identifying materials containing >10 nCi/g. The amount of material containing >10 nCi/g that would be treated is estimated to be 7,000 m^3. The concentrated waste product requiring long term storage would be stored in a module that meets requirements of the Resource Conservation and Recovery Act (RCRA) and other Applicable or Relevant and Appropriate Requirements (ARARS).

DESCRIPTION OF REMEDIAL TECHNOLOGIES

The processes proposed by the two teams include technologies used in other applications. Lockheed's TRUclean process, used for decontamination of soils, has been successfully demonstrated on a pilot and full-scale basis in various applications including operation on plutonium contaminated soils surrounding the LE-1 facility on Johnston Atoll. In addition, Lockheed's B.E.S.T. process is the best demonstrated available technology for removal of hazardous organics from soils and sludge, and will be adapted for application on plutonium contaminated soils through the Pit 9 POP. WMES' ACT*DE*CON process, used for removal of actinides from soils, was successfully demonstrated for the DOE in 1991 and WMES' PO*WW*ER system is proven technology involving evaporation and catalytic oxidation technologies. In sum, each of the proposals consist of unique combinations of chemical extraction, physical separation, and stabilization technologies for treatment of transuranic contaminated waste as described in the following section.

WMES Process Description

Figure 1 depicts the simplified WMES process system.

Retrieval/Physical Separation System. Under this approach, hazardous substances would be retrieved in a fixed, concrete, double-containment structure under negative pressure built over the entire pit at the start of the project. The pit would be worked using remotely operated excavating equipment enclosed in a curtained area to separate the excavation area from the rest of the pit. The curtained area enclosure would confine contaminated dust and volatile organic contaminants at the dig site. The excavator and associated manipulating equipment would perform an initial segregation of waste materials in the pit into five waste streams: combustibles (paper, plastics, and rags), wood, drums and metals, soil and sludge, and non-soils and large items. This initial segregation would simplify the overall material handling and processing systems downstream.

A dig face radiation monitor would be used to make a gross radioactivity level assessment of the waste at the dig face during excavation activities. The radiation monitor would have sufficient mobility to allow placement within a few inches of any area of the dig face. The readings would determine how the material

would be handled as it is excavated. If readings are high, the material would be mixed with scoops of lower reading material. In this way, overall treatability of the material would be enhanced and chance of criticality minimized.

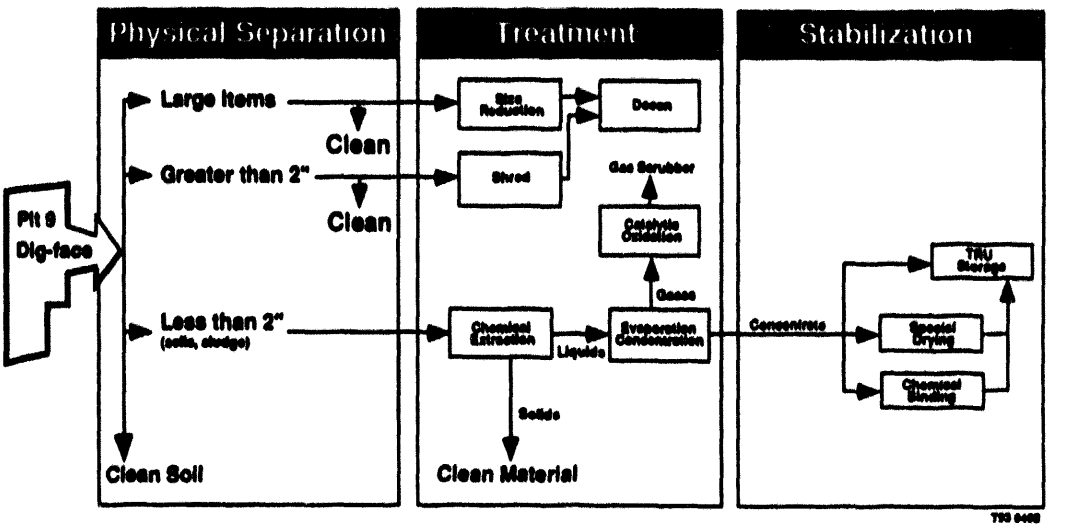

Figure 1. Waste Management Environmental Services, Inc. process (simplified).

Following initial segregation, wastes would be placed in specialized, color-coded tram containers. The containers would then enter the waste transport system, which includes a conveyer system for transporting the trams to the material handling facility from the dig site. Additional retrieval system process equipment includes a compactor to compact drums, a specialized grapple to pick up drums and drum remnants, and teleoperated manipulators to perform waste handling and segregation tasks in the pit such as cutting and drilling. Once wastes arrive in the material handling facility they would be segregated (using remotely controlled equipment) into separate waste streams at multiple handling stations. Operations performed include:

- Segregation of the waste for processing or storage
- Size-segregation of the soil and sludge wastes (to less than 2 inches) for processing in the treatment system described below
- Delivery of treatable soils to the processing facility for treatment
- Compaction of appropriate waste to minimize volume
- Shredding and sizing of large items and combustibles (including wood, metals, rags, paper and plastic) prior to decontamination in a specialized washing process

Materials contaminated with polychlorinated biphenyls (PCBs) would be segregated and accumulated until a sufficient volume is collected to permit cost effective treatment. The PCBs would then be destroyed in a proprietary dechlorination process which chemically converts the PCBs to a non-hazardous form.

Treatment System. Waste materials that are less than 2 in. in size (including contaminated soil, sludge, and non-soil wastes) would be sent to the treatment system for processing. The proposed treatment involves three principal subsystems. The extraction subsystem includes a proprietary carbonate/ethylene diamine

tetra-acetic acid (EDTA) chemical leach system for removing actinides (plutonium and americium) and heavy metals from the soil. Dissolution effectiveness is affected by soil size, feed makeup, and contact time. This subsystem also includes a surfactant-enhanced soil wash system for organics removal. The primary function of the extraction subsystem is to move the contaminants from a solid to aqueous phase.

Extraction system overflows and slurries would be routed to the filtration subsystem consisting of a clarifier, filter tank, and filter press. Clarifier sludges would be sent to the filter tank for preparation before entering the filter press. After processing in the filter press, the solids would be separated from the liquids, and a high solids (60% or greater) filter cake would be produced. Near the end of the filtration cycle, cleaned process water would be used for a final wash of the pressed cake prior to discharge. The dried solids from the filter press should meet cleanup standards of <10 nCi/g TRU. If not, they would be recycled for additional extraction. The filtrate from the filter press would be returned to the extraction subsystem.

Clarifier overflow, which should contain plutonium, americium, heavy metals and organics, would be sent to a final proprietary subsystem consisting of an evaporator, a catalytic oxidizer and a scrubber/condenser. The evaporator concentrates and volume-reduces the process water (from the clarifier feed) into volatilized and non-volatilized fractions. The organics in the volatilized fraction would be destructively oxidized resulting in a "pure" water stream which could be reused in the process, or eventually discharged along with some CO_2 gas. Off-gases from the oxidizer would be wet scrubbed. The nonvolatilized fraction, referred to as "waste product," contains nonvolatile organics, concentrated salts, heavy metals and radionuclides. The waste product would contain a solids fraction around 65% depending on the nature of the feed. If necessary, the waste product would undergo a stabilization process prior to packaging in drums for TRU storage. The waste product would meet the RWMC waste acceptance criteria, or, in the event that the hazardous waste materials are present, the waste product would meet ARARs.

Chemicals and liquids used in remediation would be recycled, thereby minimizing wastes from the process itself. Chemicals, liquids, filters, and other contaminated material left after the Pit 9 action is completed would be processed through the treatment system as a waste stream. The resulting waste would be stored as TRU contaminated waste. No liquids would be left from the process.

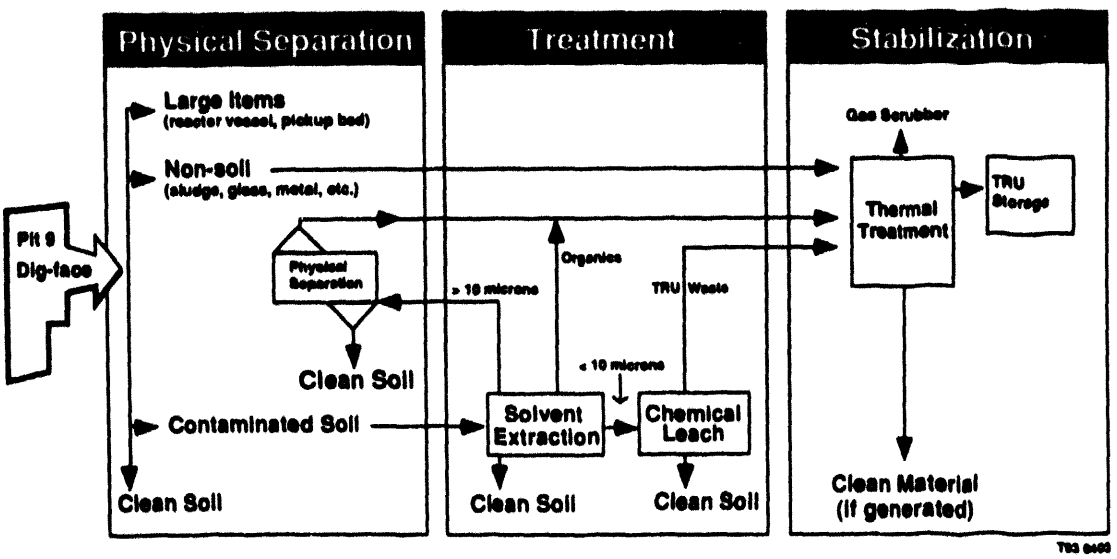

Figure 2. Lockheed process (simplified).

Lockheed Process Description

Retrieval/Physical Separation System. Under this remedial process, retrieval would be performed inside a movable, redundant containment structure with a flexible skirt and a remote teleoperated bridge crane system to prevent dispersion of contaminants into the environment and to protect operators/workers from exposure to radiation, hazardous substances and other hazards associated with excavating the pit. Separated materials would be transported from the pit to the processing building via an enclosed track in sealed containers on wheeled carts.

Inside the process building, the containers would be stockpiled awaiting processing in an area served by a bridge crane for handling. Contaminated soil would be separated from non-soil wastes and inventory tracking would be maintained using codes on the containers which identify the content of fissile material and all special handling requirements.

Treatment System. Soil processing would begin with removal of volatile organic compounds using a low temperature solvent extraction with triethylamine followed by gravimetric and physical removal of particulate plutonium and americium from the coarse soil fraction. The fine fraction which exits the gravimetric system in the tailings would be leached with nitric acid to dissolve the contained plutonium and other hazardous materials. The metal nitrates in the resultant solution would be removed using a countercurrent ion exchange system.

The "clean" soil would be transferred from the leach circuit after dewatering to a rotary kiln to remove residual nitrates. Nitrate-bearing liquid process wastes would be treated by electrodialysis for recovery of nitric acid, sodium hydroxide, and cleaned water. These materials would be returned to the process. The concentrated residues from this system would be transferred to the plasma melter for stabilization as a cast slag. After denitrification, the soil would be sampled, stockpiled until analysis verifies clean up criteria are met, and then redeposited in the pit.

The non-soil wastes and the residual concentrates from the soil treatment system would be sent directly to the plasma melter, which would destroy the organics and produce a virtually non-leachable cast slag that immobilizes both the heavy metals and transuranics. To prevent the possibility of plutonium release with the process off-gases, the melter would be equipped with an emissions control system that employs high-temperature cross flow sintered metal or ceramic filters to capture plutonium particles after condensation, scrubbers to abate acid gases, and HEPA filters. All of the plant emissions would meet the requirements of the Clean Air Act. A final radioactive/ non-radioactive sort would then be made on the plasma furnace slag to determine whether to return it to Pit 9 or to store it as a TRU waste.

Chemicals and liquids used in remediation would be recycled, thereby minimizing wastes from the process itself. Chemicals, liquids, filters, and other contaminated material left after the Pit 9 action is completed would be processed through the treatment system as a waste stream. The resulting waste would be stored as TRU contaminated waste. No liquids would be left from the process.

RELATIONSHIP TO EARLIER INEL RETRIEVAL EFFORTS

During the late 1970s, waste was retrieved and stored at the SDA in association with the Initial Drum Retrieval (IDR) and Early Waste Retrieval (EWR) Projects (8,9). The IDR program was initiated in FY - 1974 to retrieve drums buried between 1968 and 1970. IDR efforts led to the retrieval of 20,262 drums with a TRU waste volume of 4391 m^3 and 1 m^3 of contaminated soil. IDR retrieval operations were limited to SDA Pits 11 and 12, which contained drums of good integrity and only limited external contamination. Most of the retrieved waste was repackaged and stored on 20-yr. interim storage pads.

The EWR project began operations in FY 1976 to investigate methods, risks, and hazards associated with the retrieval of 65,000 m^3 of transuranic contaminated waste in below grade storage. The EWR retrieval efforts were conducted in SDA Pits 1 and 2 and in trenches 5, 7, 8, 9, and 10. Waste retrieved during EWR included drums, loose waste, and contaminated soil. Approximately 67% of the drums retrieved were severely breached.

The early retrieval efforts were conducted using only limited confinement systems and involved direct handling and excavation of the waste by workers. Both retrieval operations used Air Support Weather Shield structures to protect workers, retrieval equipment, and instrumentation from weather. The EWR project also used a negatively pressurized Operating Area Confinement structure to prevent contamination spread to the environment. Personnel protective clothing used for IDR was limited to anticontamination (anti-C) equipment including coveralls, shoe covers, and gloves. Workers carried respirators in the advent of an airborne contamination release. EWR retrieval personnel wore full anti-C clothing and a totally enclosed bubble suit that incorporated a fresh air supply. Neither of the early retrieval projects included monitoring for organic chemicals.

Also associated with the IDR project was limited excavation and probing of Pits 6, 9, and 10. Results of the probes showed wastes in Pit 9 to be in relatively poor condition, associated with high levels of loose alpha contamination, and associated with high risk of contamination spread if retrieved under the IDR program. Lessons learned from the early retrieval projects included:

- Safe retrieval of intermixed waste buried for more than 10 yrs. is not possible using methods similar to those used in the IDR program
- Future retrieval operations should not involve methods requiring direct contact with waste by retrieval personnel
- Future retrieval operations should have the capability of immediate waste encapsulation
- Retrieval equipment/buildings should be designed for ease of decontamination
- Early retrieval efforts support the concept of using mechanized retrieval equipment to achieve necessary retrieval rates and worker isolation

The Pit 9 project has been structured to incorporate many of the design recommendations from the IDR and EWR projects. Wastes in Pit 9 should be similar in condition and contamination levels to those uncovered during the EWR project. The retrieval system in Pit 9 will be designed to be isolated, mechanized, and remotely operated. Safety considerations will address organic chemicals hazards in addition to hazards associated with radioactive materials.

SUMMARY

The Pit 9 Interim Action is being conducted under CERCLA in support of the INEL SDA remediation and will reduce the risks associated with the potential migration of Pit 9 wastes to the Snake River Plain Aquifer. The tiered project approach supports demonstration of private industry's capabilities for remediating transuranic-contaminated mixed waste sites while minimizing costs to the DOE. The cost and cleanup effectiveness of the proposed technologies will be demonstrated through proof-of-process and limited production testing of critical and integrated process systems. Information gained from the testing phases will be factored into the final cleanup system which will treat the major risk drivers within Pit 9 sufficiently to minimize or eliminate remediation following the interim action.

The additional approach of two teams competing during the POP test phase allows continued development of two viable remediation technologies. It also allows continued competition on the project and the associated benefits, and enables the original procurement framework to be followed. The project strategy

enables public concerns regarding proven technologies to be addressed and to demonstrate that the project will be conducted in a safe, professional, and cost effective manner.

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SUMMARY OF FY 1992 OPERATIONS OF THE VAPOR EXTRACTION SYSTEM AT THE HANFORD SITE, WASHINGTON

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ABSTRACT. The 200 West Area Carbon Tetrachloride Expedited Response Action is being conducted on the Hanford Site by the U.S. Department of Energy at the direction of the U.S. Environmental Protection Agency and the Washington State Department of Ecology. The Expedited Response Action was initiated based on concerns that carbon tetrachloride residing in soils beneath the 200 West Area from past disposal practices may be continuing to serve as a source for contamination of the groundwater. The method for removing the carbon tetrachloride includes utilization of soil vapor extraction from existing wells with above-ground collection of the carbon tetrachloride on granular activated carbon. The activated carbon is sent off-site for regeneration. This paper summarizes the operations and lessons learned for Fiscal Year 1992 and presents operational plans for FY 1993.

INTRODUCTION

The Hanford Site, operated by the U.S. Department of Energy (DOE), covers approximately 560 mi^2 in southeastern Washington State. The Hanford Site was established in 1943 to produce plutonium for weapons, using nuclear reactors and chemical processing plants. Aqueous and organic low-level radioactive wastes from chemical processes were discharged directly to soil column disposal sites located throughout the Hanford Site. Within the 200 West Area, large quantities (estimates range from 400,00 to 580,000 L of liquid waste containing carbon tetrachloride (CCl_4) and radionuclides were discharged from the Plutonium Finishing Plant to three such disposal sites. As a result of past disposal practices, concentrations of 100 times the maximum contaminant level (MCL) for CCl_4 have been detected dissolved in groundwater more than one-half mile upgradient of the disposal sites. It has been estimated that the CCl_4 dissolved contamination in the groundwater extends approximately seven square miles.

On December 20, 1990, the U.S. Environmental Protection Agency (EPA) and Washington State Department of Ecology requested the DOE to assess contamination and evaluate alternatives for an Expedited Response Action (ERA) for CCl_4 contamination located in the unsaturated soils beneath certain disposal sites in the 200 West Area. The request was based upon concerns that the CCl_4 residing in the soils were continuing to spread to the groundwater. An ERA allows expedited responses to be taken at waste sites where early remediation will abate imminent hazards or prevent significantly increased environmental degradation that might occur if action were delayed until completion of a remedial investigation/feasibility study (RI/FS) and Record of Decision.

Based on results of a vapor extraction system (VES) pilot test conducted in the spring of 1991 and an engineering evaluation/cost analysis (EE/CA), the EPA issued an action memorandum directing initiation of the ERA in a two-phased approach. The first phase of the project included production scale testing and removal of the carbon tetrachloride from the source zone using VES technology, and was initiated in

February, 1992. The second phase of the project included increased production with the use of additional extraction units and was initiated March, 1993. The proposed action for removing the CCl_4 in the unsaturated soils includes utilizing soil vapor extraction technology with aboveground collection of the carbon tetrachloride on granular-activated carbon (GAC). The GAC is then sent offsite to be regenerated and the carbon tetrachloride destroyed. This paper summarizes operations and lessons learned for Fiscal Year (FY) 1992, and presents operational plans for FY 1993 for the VESs used on the Hanford Site, Washington.

SYSTEM DESCRIPTION

There are currently three vapor extraction systems utilized on the Hanford Site for extracting CCl_4 from the unsaturated soils: a 500 ft^3/min unit, a 1000 ft^3/min unit, and a 1500 ft^3/min unit. All three VESs share a common system design. The extraction system(s) consist of two mobile trailers; a High Efficiency Particulate Air (HEPA) filter trailer and a Vacuum Blower trailer. The general function of the two trailers is to create the vacuum necessary to extract the CCl_4 laden soil gas from the well field, remove moisture and particulates from the soil gas, disburse it to a collection system to strip the CCl_4 from the soil gas, and then release the remaining gas to the atmosphere. Figure 1 illustrates the general layout of the VES trailers.

The HEPA filter trailer contains a well intake manifold for connection to four wells, with the capability to expand to eight wells, a water separator, a HEPA filter assembly that includes preheaters, appropriate differential pressure instrumentation, sampling and lighting, valving and control instruments.

The Vacuum Blower trailer contains three vacuum blowers (depending on the system design), an outlet distribution manifold to allow connecting with hoses to three GAC canisters in series, intercanister pipe segments with monitoring instrumentation, a return manifold from the GAC trains, a control room housing a Process Control System including a work station, and an electrical power distribution system and instrumentation.

The system design utilizes chlorinated hydrocarbon, radon, and continuous air monitors (CAMs) for monitoring the effectiveness of the VES and to assure meeting regulatory discharge limits. The design of the systems used on the Hanford Site go beyond the typical volatile organic VES due to the radionuclides that were disposed concomitant with the carbon tetrachloride. There is concern of the potential for extracting alpha particulates, thus the need for HEPA filters and radionuclide monitoring instrumentation (CAMs and a record sampler). In addition, the build-up of naturally occurring radon in the GAC canisters is monitored to assist in releasing the canisters for off-site regeneration.

SITE DESCRIPTION

The unsaturated zone underlying the three disposal sites ranges from approximately 60 to 66 m thick and consists primarily of sands and gravels. A relatively impermeable fine-grained zone approximately 10 m thick occurs at 40 m below. It is suspected that this impermeable zone may temporarily divert or perch dense liquids and vapors, such as CCl_4, and now appears to be associated with the highest observed concentrations of CCl_4. During 1992, 17 existing wells at two of the disposal sites were perforated at various intervals above the impermeable, fine-grained interval to provide subsurface access for vapor extraction.

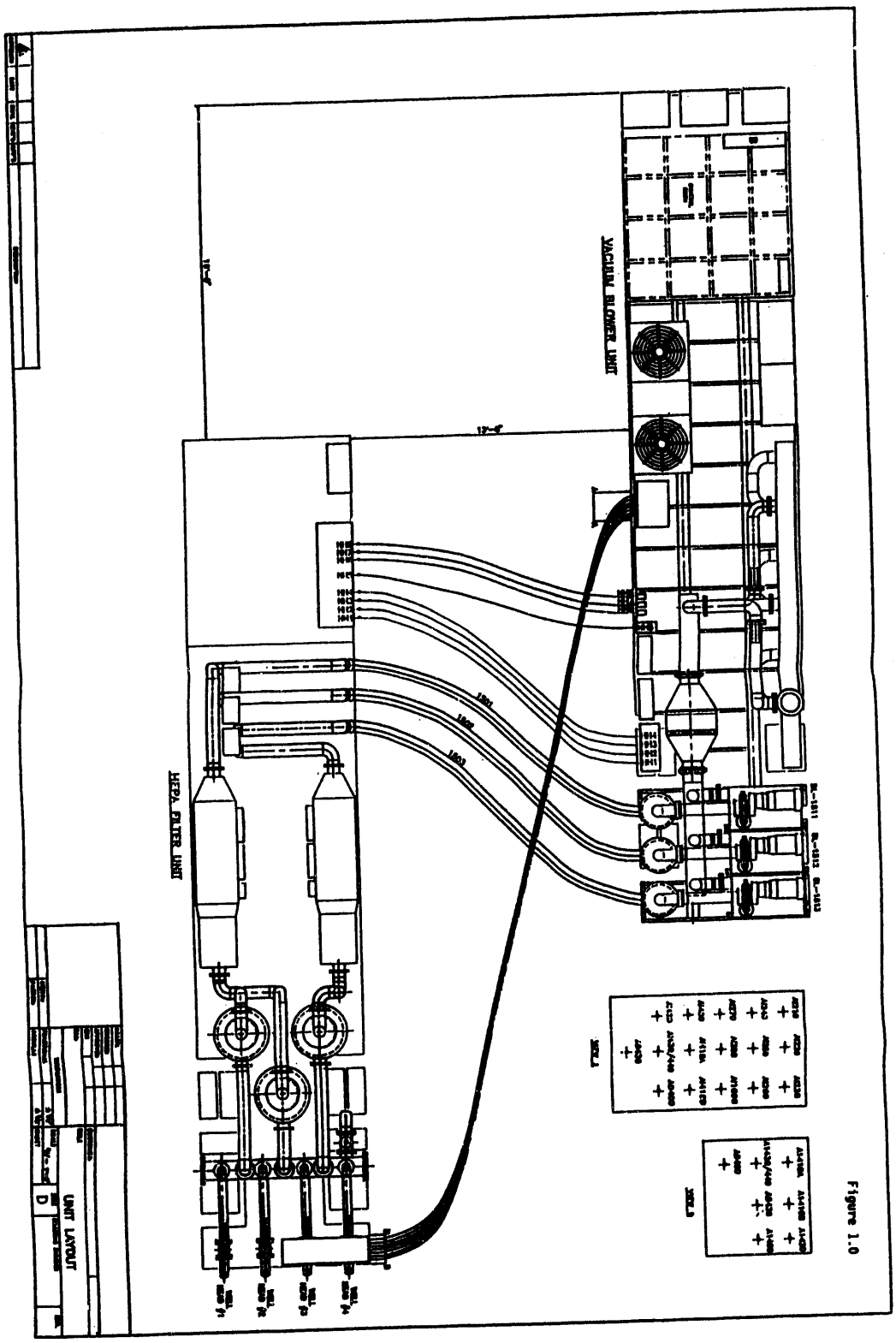

Figure 1

WELLFIELD MONITORING

Monitoring of the well field used for extraction purposes focuses on measurements of vacuum and flow at the wellhead. Pressure and flow indicating transmitters are located on each wellhead to provide information on the vacuum and flow developed at each well. Sampling points are located at specific depth intervals within wells selected for use in vapor extraction operations. Both monitoring and extraction wells may be used in vapor extraction operations. The well to be used for extraction is connected by a hose from the wellhead to the HEPA trailer. Vacuum and flow measurements are also monitored at the intake manifold located on the HEPA trailer with control of the system vacuum performed on the HEPA trailer manifold. Data collected during well field monitoring is transmitted to the data acquisition system for computer storage and use. These data include continuous measurements of wellfield vacuum and flow. The well field data are used primarily for trending analysis, studying the effect of varying carbon tetrachloride concentrations, and flow rate and depth in the extraction well on the vacuum pressures in monitoring wells. The data acquisition system is capable of receiving data at all times during operation and of transmitting either the real time data as they are received or historical data.

OPERATIONAL AND PROGRAMMATIC ACCOMPLISHMENTS FOR FISCAL YEAR 1992

Significant accomplishments for the year included initiation of operations in fulfillment of Phase I of the project (as required per EPA Action Memorandum), downgrading the radiological protection controls required to operate the system(s), expansion of the existing wellfield, the award of several key procurement contracts, and successful integration of the project team. Each of these accomplishments are further discussed below.

Initiation of Operations

The first of three planned VESs, a 500 ft^3/min unit, was placed in operation on February 25, 1992. During Fiscal Year (FY) 1992 approximately 1900 pounds of CCl_4 were extracted from two disposal sites. Fluctuations in CCl_4 concentrations from different wells were encountered, ranging from 75 ppm to 2000 ppm due to differences in the morphology and geology of the soils and the ability of the VES to induce flow from the wells. The fluctuation in concentration and flowrate accounted for a variation in the loading rate of the GAC canisters. Table 1.0 illustrates the effect of various concentrations and flows on the GAC loading rate.

Table 1. Production based on capacity and concentration.

FLOW	100 PPM	1000 PPM
500 ft^3/min	28 LBS/DAY	280 LBS/DAY
1000 ft^3/min	57 LBS/DAY	570 LBS/DAY
2500 ft^3/min	141 LBS/DAY	1410 LBS/DAY
3000 ft^3/min	170 LBS/DAY	1700 LBS/DAY

Downgrading Radiological Protection Controls

At the three disposal sites, past waste disposal practices consisted of discharging radionuclides concomitant with aqueous wastes containing CCl_4 to the soil column. The initial planning for the ERA included assessing future VES operations and determining the appropriate level of radiological protection controls required to operate the system. The original determination was to apply strict contols, such that the entire system was determined a radiological control zone.

Based on results of the pilot test, no radionuclides were detected either during or after completion of the test. After completion of an indepth safety analysis, the radiological protection controls were relaxed to reflect realistic radiological conditions. Through operational experience and safety assessments the Westinghouse Hanford Company has been successful in downgrading radiological controls required to operate the system. There are currently three main radiological control areas around the system: the GAC canisters, the well intake manifold, and the HEPA filter(s).

Procurement

During FY 1992, several key procurement contracts were awarded that were instrumental for increasing future extraction capabilities. The large 1500 ft^3/min VES specification was prepared and awarded as well as activities were initiated to procure another 500 ft^3/min VES and upgrade the existing 500 ft^3/min VES to 1000 ft^3/min. The 1500 ft^3/min VES was specified to be a "turnkey" procurement whereby the system would be constructed and assembled onsite. Implementation and completion of these activities would provide a total extraction capacity of 3000 ft^3/min resulting in the average removal rate of 1000 lbs/day of CCl_4.

Wellfield Expansion

Six new vapor extraction wells were completed during FY 1992 to optimize extraction capabilities. Three of the wells were located adjacent to the disposal sites extracted in 1992, and have one screened interval above the impermeable fine-grained layer. The remaining three wells were located approximately 20 to 40m from the disposal sites and have two screened intervals; one above and below the fine-grained layer.

Project Team

The successes of FY 1992 would not have been accomplished without the implementation of a project team that consisted of personnel from several companies and organizations. Each individual on the project team understood the relative importance of the project and took ownership and responsibility in his/her tasks to ensure completion of them in a timely fashion. The primary key to success of the project was effective communication between all parties involved.

LESSONS LEARNED

Lessons learned from operation of the VES during FY 1992 include: a need for continued development of a chlorinated hydrocarbon process control monitor, a need for enhanced monitoring/understanding of the fate of radon in the natural environment, and the need to gather nonradiological ambient air baseline data. Each of these items are further discussed below.

Chlorinated Hydrocarbon Detector

Efficiency of the VES is measured by monitoring the concentration of carbon tetrachloride before the GAC canisters, between the GAC canisters, and after the last GAC canister. The GAC canisters are considered loaded when they are 25% saturated with CCl_4. Since each of the canisters contain 2000 lbs of carbon, a

loaded GAC canisters would contain 500 lbs of CCl_4. Therefore, measurement of breakthrough in the canisters is critical in assessing the removal efficiency of the GAC and determining when to change the canisters.

Initial process control monitoring instrumentation consisted of an organic vapor monitor. Unfortunately, the monitor does not have the capability to detect low concentrations of CCl_4 and is adversely affected in high concentrations of CCl_4. In response to this problem, an indepth search was conducted to find a monitor that could operate effectively in a wide range of concentration levels. Although a substitute monitor was discovered that could withstand the wide range of concentrations encountered during operations, the monitor is not user friendly and is still in the research and development stage. As a result, an alternative monitor is still being aggressively sought that could provide field personnel with quality information that is easily operated.

Radon in the Environment

In the process of extracting CCl_4 from the vadose zone, radon gas is also extracted. Since radon is a noble gas it is extracted in addition to the carbon tetrachloride and adsorbed on the GAC. During VES operations, it has been observed that the GAC has a higher affinity for CCl_4 than for radon. The VES operates with three GAC canisters in series. It has been observed that as the primary canister is receiving CCl_4 there is an increase in radon which is exhausted to the secondary canister. This pattern is carried through to the other canisters. Theoretically, when the primary canister reaches breakthrough an increase in radon concentration should be observed in the third canister. Assuming this theory holds true, radon could be used as a process indicator for when to change the canisters. This could be of relative importance given the lack of a reliable CCl_4 monitor. In addition, further research is needed to investigate whether there is a relationship between the concentration levels of CCl_4 and radon.

Nonradiological Ambient Air Data

Prior to initiation of VES operations, a new type of chlorinated hydrocarbon detector was being tested in ambient air at the ERA site. During testing of the monitor concentrations of chlorinated hydrocarbon were detected at levels near the Permissible Exposure Level for CCl_4. Following discussions with our Environmental Protection Organization it was discovered that nonradiological constituents are not monitored in ambient air on the Hanford Site. As a result of this incident, personal exposure monitoring has become an important part of our safety program, along with an increased need to monitor ambient air at the ERA site.

OPERATIONAL AND PROGRAMMATIC OBJECTIVES FOR FISCAL YEAR 1993

Operational and programmatic objectives for FY 1993 for the 200 West Area ERA included implementation of two additional VESs, upgrading the existing VES to 1000 ft^3/min, maximizing production from the various wellfield(s), and optimizing the loading of CCl_4 on the GAC. Fulfillment of these objectives would complete Phase II of the project.

To date, operations of two additional VES units, a 500 ft^3/min and a 1500 ft^3/min unit, have been initiated at the third disposal site. In addition, the original VES has been upgraded from 500 to 1000 ft^3/min to support expanded operations. Initial testing of existing wells at the third disposal site indicate CCl_4 concentrations up to 30,000 ppm. These concentrations have been observed originating from the fine-grained layer of the subsurface. Four of the wells at the third disposal site are planned to be perforated in the coarser soil above this layer, to improve air flow across the top of the fine-grained layer. If feasible, an additional four wells below the impermeable zone will also be perforated to optimize extraction operations.

During FY 1993, up to 10 new extraction wells are planned to be drilled in support of the ERA. Two of the wells will be screened just above the fine-grain interval and will be located within the CCl_4 disposal sites. Outside the disposal site(s) perimeters, up to seven dual-screened extraction wells are planned. In addition, an angle hole well is planned to be drilled to provide access beneath a parking lot where soil gas surveys have indicated high CCl_4 concentrations.

Fourteen locations have been selected for installing wells utilizing a cone penetrometer. These wells will be designed for extraction, monitoring, and/or air injection purposes. The wells will also allow monitoring of subsurface soil gas concentrations and pressures. The target depths for these wells will be above the fine-grained interval.

Because the success of vapor extraction operations is dependent upon understanding and controlling air flow in the subsurface, a study of the subsurface air flow pathways is planned for FY 1993. The study will evaluate existing VES extraction and monitoring data and will include tracer gas testing. The tracer gas tests will be conducted using an inert, non-toxic tracer gas and will be used specifically for determining subsurface air flow pathways, the rate of transport of the contaminant vapor, and the radii of influence of the extraction wells.

Production data from the VES and determination of the radii of influence and air flow pathways will be combined with other site data to determine the wellfield strategy for each disposal site. The strategy will include recommended flowrates, extraction locations, and other air flow control functions, and will be adjusted to optimize use of the wellfield as conditions change and additional information is obtained through operations, monitoring, and analysis.

The 200 West Area CCl_4 ERA is projected to continue through FY 1995. The total amount of carbon tetrachloride to be removed from the vadose zone is estimated to be 600 metric tons. The use of VES technology has proven to be an effective technology in removing carbon tetrachloride from the vadose zone on the Hanford Site.

MAWS: A PROGRAM FOR THE DEVELOPMENT AND DEMONSTRATION OF AN INTEGRATED, MULTIPLE-TECHNOLOGY, MULTIPLE-WASTE-STREAM TREATMENT SYSTEM FOR THE FERNALD SITE

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ABSTRACT. The Minimum Additive Waste Stabilization (MAWS) Program is scheduled to demonstrate an integrated-system (vitrification, soil washing, and water treatment) approach to the treatment of multiple waste streams at the Fernald site, beginning in mid-1993. This paper discusses the major concepts underlying the MAWS approach, the main objectives of the program, and the progress that has been made to date. A soil washing process has been developed that achieves substantial volume reductions while producing a contaminant-enriched fraction suitable for blending with other waste streams to produce a vitrifiable feed. Glass-based waste forms have been developed for Fernald mixed waste blends that show excellent leach resistance, are processable using improved joule-heated vitrification technology, and achieve very high waste loadings. The large volume reductions obtained with this approach translate into substantial reductions in life-cycle remediation costs. These benefits should be widely applicable to other sites.

INTRODUCTION

The Minimum Additive Waste Stabilization (MAWS) Program includes the development and on-site demonstration of an integrated, multiple-technology system to treat blends of several waste streams. Such an approach has great potential for achieving significant reductions in overall treatment and disposal costs. The field demonstration will be conducted at the Fernald Environmental Management Project (FEMP) site beginning in mid-1993. The program is supported jointly by the U.S. Department of Energy (DOE) Office of Technology Development and Office of Environmental Restoration through a prime contract to GTS Duratek Inc., with Lockheed Environmental Services Corporation (LESC) and The Vitreous State Laboratory (VSL) of The Catholic University of America as subcontractors; on-site support is provided by FEMP management (FERMCO) and their subcontractors. Contract management and technical support related to wasteform leach resistance evaluation is provided by Argonne National Laboratory (ANL). While FEMP is the focus of the MAWS program, the benefits should extend to many other remediation sites.

The MAWS system integrates three primary technologies - vitrification, soil washing, and water treatment - to address a variety of waste streams, including mixed wastes. The system is centered around a vitrification system which will direct all contaminant streams to a stabilized glass waste form. Vitrification was selected as the stabilization technology due to the superior leach resistance of the waste form and the large volume reduction compared to many alternative technologies. Large volume reductions translate directly into significantly reduced life-cycle remediation costs.

The MAWS concept is innovative in several respects: the available waste streams are viewed as resources for the process; the chemical properties of these resources are fully exploited to minimize the need for the

purchased additives usually required for stabilization; and a portfolio approach is adopted to maximize the economic benefits of blending the optimum proportions of multiple waste streams in an integrated system composed of an appropriate combination of treatment technologies.

These general principles are widely applicable to a variety of remediation problems. However, different system configurations and treatment-technology combinations may be more appropriate as the types and relative volumes of the waste streams involved change from site to site. The specific MAWS system described here was developed for the Fernald site where the major waste streams are pit sludges and contaminated soils and waters.

THE FERNALD SITE

The Fernald site produced uranium and thorium from the early 1950's until 1989, after which time the mission became one of environmental remediation. A variety of chemical and metallurgical processes were used at Fernald and have resulted in the accumulation of large volumes of process wastes and associated site contamination. Major process operations included the dissolution of uranium-bearing starting materials in nitric acid followed by solvent extraction to yield uranyl nitrate. The acid wastes, containing a variety of heavy metals and radionucleides, were neutralized with lime which precipitated the majority of the contaminates as a sludge which was pumped to open pits. The uranyl nitrate was converted in a sequence of steps to UO_3, UO_2, UF_4, and UF_6. Uranium hexafluoride was used for subsequent enrichment by gaseous diffusion off site. The uranium fluorides were ultimately reduced to uranium metal by reaction with magnesium metal at Fernald. The magnesium fluoride wastes produced in this step were also directed to the sludge pits. While various other process wastes were also directed to these pits, the bulk of the pit wastes are expected to be high in calcium, magnesium, and fluorine with heavy metal and radionucleide contaminants. The total volume of these sludges is estimated to be about 470,000 yd^3. There is about 690,000 yd^3 of contaminated soils, at least 2.3 million gallons of contaminated surface water as well as the fly ash, asbestos, and transite wastes that are characteristic of many DOE sites. In addition, large quantities of high specific activity radium-bearing wastes, generated from pitchblend processing, are stored in concrete silos on the Fernald site.

A number of technologies are under consideration for treatment of the pit wastes including cementation, vitrification, and polymer stabilization. Since the Record of Decision for the FEMP Operable Unit 1 (waste pit area) is December 1994, there is a window of opportunity for demonstration and evaluation of innovative treatment concepts. The MAWS approach draws upon available treatment technologies and integrates them into a treatment system that can address multiple site waste streams in such a way that the overall treatment cost are reduced in comparison to treating each stream separately. The MAWS system for FEMP will focus initial efforts on Pit 5 sludge and contaminated soils and water. The development and demonstration activities will be subsequently expanded to include other site waste streams.

THE MAWS SYSTEM

Figure 1 shows a schematic representation of the MAWS system for FEMP; other pretreatment systems (e.g. incineration for waste that are very high in organics) could be employed in alternative system configurations. A major system objective is to produce a single highly leach resistant waste form and releaseable ("clean") effluents only, i.e. no side stream wastes. Vitrification was selected as the best available technology around which to build this system for a number of reasons:

- There exists a well-developed technology base from high-level waste programs and the commercial glass industry
- Large volume reductions are achievable

- Thermal processing destroys organic contaminants
- Ability of glass to chemically incorporate a wide range and large amounts of hazardous and radioactive components
- A stable homogeneous wasteform is produced that can be made highly resistant to aqueous corrosion
- The waste form material is similar to many natural minerals whose long-term corrosion resistance has been demonstrated by the geological record.

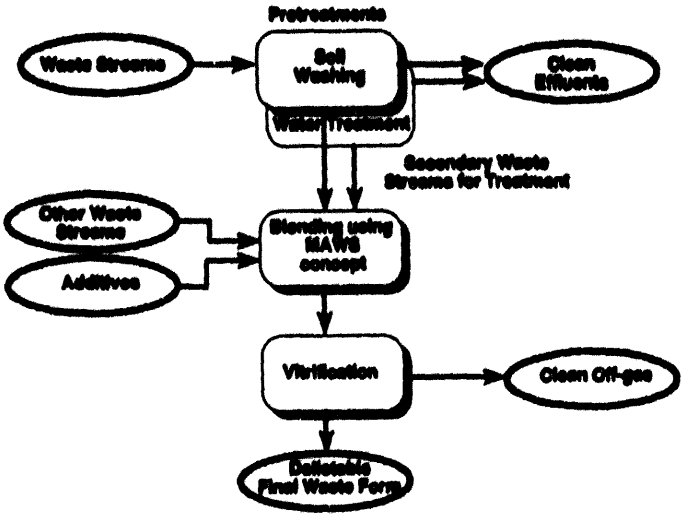

Figure 1. MAWS integration of multiple technologies.

The potentially very high leach resistance of a glass-based waste form for FEMP mixed and low-level wastes is especially attractive in light of the fact that several of the pit wastes are RCRA listed wastes. In these instances it is likely that a very strong case can be made for delisting the vitrified wastes which would result in significant further savings in disposal and monitoring costs.

From a vitrification perspective, waste streams can be broadly classified on a spectrum of silica-rich to flux-rich; these extremes having opposite effects on melt temperature and viscosity. Due to the very large volume of uranium-contaminated soils at FEMP, the total waste mix will be dominated by the silica-rich components; this is a common situation at many remediation sites. Treatment of the soils alone would typically require addition of fluxing agents which are an additional expense and diminish the volume reduction. In the MAWS blended-waste-stream approach, the FEMP pit sludges play the role of the required fluxing agents. The silica:flux balance in the blended steam is improved by volume reducing the uranium-contaminated soils by treatment in a soil washing process. The contaminant-enriched minor fraction (about 20%) is then used as feed for the vitrification process by blending it with other streams. The soil washing process requires large volumes of water which becomes contaminated in the process; contaminated site water can be used for this purpose. The uranium contamination is removed from this water by an ion exchange water treatment system which treats water to discharge standards and recycles back to the soil washing system. A regeneration cycle is employed to strip the uranium from the ion exchange media and direct it to the vitrification system. In this way no mixed-waste spent ion exchange media is produced. The soil-wash and ion-exchange concentrates are then blended with other waste streams (Pit 5 sludge, fly ash, asbestos, transite, etc.) in such a way as to minimize the need for purchased additives necessary for vitrification.

Figure 2 shows the principal process flows between system components for the FEMP MAWS demonstration. The system is based around a GTS Duratek Duramelter vitrification system with a nominal

glass production rate of 300 kg/day. This system is based on standard joule-heated ceramic melter (JHCM) technology as employed in high-level waste vitrification applications (1) but includes a number of proprietary innovations to enhance throughput rates and expand the operating envelope, as discussed further below. The system is supported by an off-gas treatment system which is again based on existing commercial technology with a number of proprietary improvements. These changes relate to the need to capture not only the hazardous and radioactive components but also the significant amounts of hydrogen fluoride produced in vitrifying these wet high-fluoride wastes. The off-gas system operates in such a way that no side-stream wastes are generated since off-gas sludges are recycled to the vitrification feed batch (with due respect for feed target composition and water balances in the system).

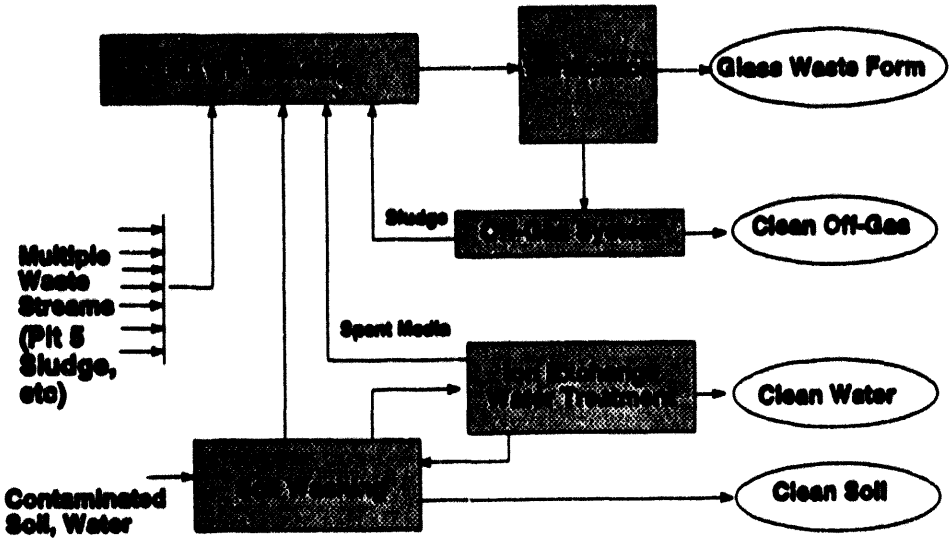

Figure 2. The MAWS system process flow.

The soil washing system is a Lockheed TRUclean system with a processing rate of about 0.25 yd^3/hr. A combination of physical and chemical processes are used including density and particle size separations and uranium leaching by mild oxidation and carbonate extraction. This system is supported by a GTS Duratek ion exchange water treatment system with a 100 gallon/min. throughput capacity.

Since FEMP Pit 5 sludge has a high water content (about 71 wt%) and a major objective is to target high waste loadings with respect to sludge, a slurry feed system to the melter was selected; a dry feed system may also be tested later in the program. The waste streams will be blended in 4000 gallon mixing tanks to produce a feed batch which will then be fed to the melter continuously. Batch preparation and feeding will alternate between the two tanks. Characterization data on the waste streams will be used to determine the requisite quantities of each, and samples from the mixing tank will be used to determine chemical additive requirements. These analytical data will be used for process control by comparison with models for the effects of composition on key glass processing parameters determined from supporting laboratory studies. Thus, process and product control is effected through control of the feed (and therefore the glass) composition. Determination of the operating envelope is discussed further below.

LABORATORY SUPPORT

Development and demonstration of the MAWS approach is supported by a variety of laboratory studies.

The VSL is responsible for the waste form design by glass composition optimization, and for a variety of analytical, glass melting, characterization, and modelling activities. Small-scale Duramelter vitrification systems are installed at VSL for laboratory tests with actual radioactive FEMP wastes. These systems have nominal glass production rates of 10 kg/day and 100 kg/day. Thus a step-wise approach is used, including crucible melts, laboratory system tests, and on-site tests, in order to extract the maximum benefit from the necessary compromise between the relatively low cost of small-scale tests and the increased realism of larger-scale tests. The laboratory Duramelter systems are used to obtain process related data, especially on off-gas emissions, that cannot be obtained from crucible melts but are critical in expediting the startup of the on-site system. Furthermore, a number of design changes have been made in the on-site system as a result of these tests.

LESC soil laboratory is responsible for the soil characterization and lab-scale testing necessary for process development and design and construction of the on-site TRUclean system. These tests also produce the soil-wash concentrates necessary for laboratory vitrification tests at VSL. A GTS Duratek ion exchange water treatment system is installed at LESC to support these tests. Loaded ion exchange columns will be provided for regeneration and vitrification tests at VSL.

Samples of the vitrified waste will be provided for detailed leach testing at ANL. These studies will employ standard (e.g. product consistency tests (PCT)) (2) as well as non-standard (e.g. vapor-phase hydration tests) (3) in order to study the potential long-term effects of the environment on the waste form and its ability to immobilize the contaminants of concern. Particular attention will be paid to formation of alteration phases and the consequences for long-term reaction progress.

WASTEFORM DESIGN AND OPERATIONAL ENVELOPE

Exploitation of the chemical nature of the waste streams that are available for blending requires optimization of the glass composition with respect to a number of imposed constraints:

- Leach Resistance - the wasteform must pass the toxicity characteristic leaching procedure (TCLP) test (4) and should also show good performance relative to high-level waste glasses on the PCT (2) since these glasses provide a well-established benchmark for comparison.
- Processability - the glass melt must have a viscosity and electrical conductivity suitable for the JHCM system employed and a liquidous temperature significantly below the processing temperature.
- Economics - the waste form must achieve a high volume reduction of the waste and a high overall waste loading (i.e. the need for additives must be minimized).

Long-term leach resistance should, of course, also be considered but this is an impractical constraint to impose early in the optimization process due to the time required to accumulate such data.

Melt viscosity and electrical conductivity constraints for JHCM processing of HLW are compared to those demonstrated with Duramelter systems in Fig 3. Constraints for high-level nuclear waste glass melts usually fall within the range of 0.15 S/cm < conductivity < 0.55 S/cm and 20 P < viscosity < 80 P for temperatures between 1100-1150°C. The viscosity bounds represent increased corrosion (<20 P) and slow throughput (> 80 P) and limitations due to the conductivity of the melter lining itself (<0.15 S/cm) and due to current density limitations of the electrodes (>0.55 S/cm). For comparison, the melt behavior of several glasses formulated from FEMP soils and sludges are also shown. The high sludge waste loadings result in high magnesium, calcium, and fluorine concentrations which produce very low viscosity melts. Considerably lower waste loading would be necessary in order to produce melts acceptable for conventional high-level waste vitrification systems. Thus, a vitrification system with an extended operating range also serves to significantly reduce additives, increase waste loadings, and reduce treatment costs.

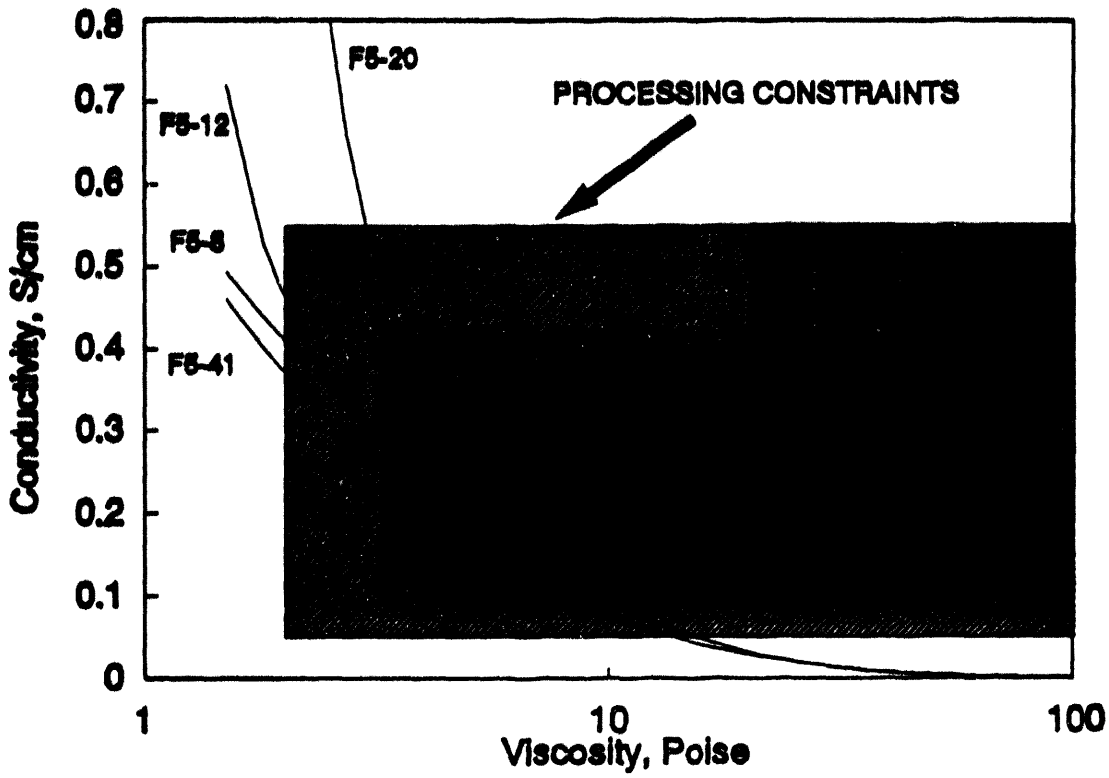

Figure 3. Processing parameters for Fernald glasses (F5-41, F5-8, F5-12, and F5-20) compared to processing constraints for JHCM vitrification systems. Curves show the experimentally determined behavior of glass melts of various compositions made from actual FEMP wastes. (Note: Temperature increases to the left along these curves).

Due to the low viscosity of these melts there is little incentive to increase processing temperatures (which reduces viscosity) in order to increase processing rates. In fact, the release of fluoride from the melt into the off-gas system provides a strong incentive to process at the lowest possible temperature. However, the tendency of the melt to form crystals below a certain temperature (liquidous temperature) provides a lower limit on the processing temperature. Excessive crystal formation produces a heterogeneous waste form and may lead to accumulation of deposits in the melter through sedimentation which may ultimately lead to clogging. It is desirable to have a liquidous temperature at least 100°C below the processing temperature to allow for temperature and composition variations during processing. However, the high concentrations of magnesium, calcium, and fluorine lead to high liquidous temperatures and, in fact, this imposes one of the tightest constraints in the composition optimization process for these wastes. Our research has shown that with small additions of B_2O_3 and Na_2O to the melt and by controlling the waste stream blend, liquidous temperatures of below 1050°C can be achieved. Examples of such feed compositions and the additives required are shown in Table 1. Notice that feed waste loadings of over 94% are achievable.

Table 1. Typical feed and resultant glass compositions for vitrification of FEMP Pit 5 and soil-wash concentrate blends.

FEED, Wt.%	F5-42	F5-46
Pit 5[a]	85	78.1
Soil-Wash Concentrates[a]	8.3	16.8
SiO_2	2	0
Na_2O[b]	1.6	1.7
B_2O_3[b]	3.1	3.4
TOTAL	100	100

(a) "As-Received" basis; (b) Sources are Sodium Carbonate, borax, and boric acid

GLASS, Wt.%	F5-42	F5-46
Al_2O_3	2.7	2.6
B_2O_3	9.8	13.3
CaO	25.4	24.1
MgF_2	25.6	24.0
Na_2O	5.6	5.6
SiO_2	26.1	25.5
Others	4.8	4.9
TOTAL	100	100

With these considerations in mind, the operational envelope is determined in large part by the variation of liquidous temperature with composition. After extensive studies on a large number of glass melts to determine the compositions of the major secondary phases involved, it has proved possible to model the composition dependence of the liquidous temperature and therefore define an important boundary of the operating envelope. The remaining boundaries are determined by the other constraints discussed above, but in general these are rather less restrictive.

SYNERGISTIC EFFECTS

A major element of the MAWS concept is that the individual system components should work together in a synergistic fashion such that the overall system is optimized; it is important to note that this is not necessarily achieved by optimizing each component separately (5). To cite a very simple example, there are a number of reasons, including economic, for using sulfuric acid for stripping uranium from the loaded ion exchange columns in order to regenerate them. However, given that a system requirement is that all contaminants are ultimately directed to the glass waste form, vitrification requirements must also be considered in this decision. In fact, sulfates can pose problems in vitrification due to their tendency to increase corrosion and their low solubility in silicate melts. For these reasons a nitric acid strip is preferred from an overall-system perspective.

A somewhat less obvious example is provided by the interaction between the soil washing and vitrification systems. Table 2 summarizes the major components (on an oxide and fluoride basis) found in FEMP Pit 5 sludge and FEMP soil and groups them broadly as "glass formers" and "fluxes". In these terms, vitrification constraints can be loosely expressed as an acceptance window of glass former:flux ratios. Pit 5 sludge is rich in fluxes whereas the soil is rich in glass formers and therefore blending is a natural approach. Unfortunately, however, FEMP soils are quite rich in calcium which would tend to

reduce the sludge waste loading achievable in the glass since the total amount of calcium that will still produce an acceptable glass is limited. Once this problem is recognized it is possible to tune the soil washing process in such a way that the contaminant-enriched fraction is also enriched in glass formers and depleted of calcium, as shown in Table 2. As a result, overall waste loadings can be significantly improved. It should be noted that this would not be the case if the soil washing process had been optimized in isolation rather than as a component in an integrated system.

Table 2. Synergistic composition effects.

	Pit 5 Sludge	Soil	Soil-Wash Concentrates
Al_2O_3	2	7.6	8.6
SiO_2	14	57	71
Glass Formers, wt%	16	64.6	79.6
CaO	37	22	9
MgF_2	40	0	0
K_2O	0.3	2	2.2
Li_2O	0.3	0.2	0
Na_2	0.9	1	1.2
Fluxes, wt%	78.5	25.2	12.4

ECONOMICS

It was argued above that blending waste streams and combining technologies into an integrated system can reduce the need for chemical additives required for vitrification and thereby reduce overall treatment costs. However, it is appropriate to also discuss the economic consequences of building the system around a glass-based waste form rather than other available waste forms. In particular, vitrification is frequently perceived as a relatively expensive technology (perhaps from its applications to high-level waste) which would not be economically competitive with alternative technologies, such as cement stabilization, for treatment of low-level and mixed wastes. However, analysis of life-cycle costs, which include disposal costs as well as treatment costs, have demonstrated (6-8) that vitrification can be more economical than cement stabilization due to the large volume reduction for the former compared to the large volume increase for the latter. Our studies on FEMP Pit 5 waste have demonstrated five-fold volume reductions on vitrification which is to be compared with results suggested by other treatability studies of at least a doubling of the volume upon cement stabilization. When volume-based disposal costs are taken into account (presently estimated at about $\$260/yd^3$ at FEMP), this more than offsets any differences in up-front treatment costs. In fact, a recent detailed analysis of the life-cycle economics of alternative treatment approaches for all FEMP pit wastes (9) shows that both up-front (design, construction, operation and maintenance) costs as well as disposal and monitoring costs are actually lower for vitrification than for cementation, to the extent that the total saving is estimated to be about \$720 M or 56%. Thus, since there is good evidence to suggest that it may actually be cheaper to produce a more leach resistant waste form and, in addition, by using the MAWS approach other waste streams are consumed by the process, the approach merits careful consideration. Furthermore, since it is likely that a much stronger case can be made for delisting a glass-based waste form, significant further savings may be possible for those pit wastes that are RCRA listed wastes.

SCHEDULE OVERVIEW

Phase I of the MAWS program began in June 1992 and runs through May 1993. This includes lab development and testing studies; lab proof of concept; design, procurement, and construction of system components; documentation and permitting; FEMP Plant 9 facility modifications to house the MAWS system; operator training; installation and operation of system components through non-radioactive vitrification system tests. Phase II is planned to begin in June 1993 and run through May 1995. This includes on-site system integration and proof of concept using Pit 5 waste; process control development; evaluation of equipment performance; evaluation of waste form performance; runs specifically designed to accumulate data in support of a delisting application; and incorporation of other FEMP wastes including some or all of transite, asbestos, Pit 3, Pit 4, and silo wastes.

SUMMARY OF PROGRAM ACCOMPLISHMENTS TO DATE

Very significant progress has been already made as of this writing (March 1993); only the salient points will be covered here. In the area of general support, the Work Plan has been prepared, reviewed by the U.S. Environmental Protection Agency (EPA), and responses to comments have been provided; modifications to the FEMP Plant 9 facility have been completed; and the operational safety assessment is in progress. Waste form development activities have led to formulations with over 94% waste loadings which produce a processable high-quality waste-form; the data obtained for this purpose provide a solid foundation for the incorporation of other waste streams into the process. Glass have been prepared from various combinations of FEMP Pit 5 waste, whole soil, soil-wash concentrates, and fly ash.

The majority of the glasses produced, covering a wide range of compositions, show very good leach resistance on the EPA TCLP test (4); most show below 20% of the regulatory limit for concentrations of the RCRA metals (Ag, As, Ba, Cd, Cr, Hg, Pb, Se) in the leachate. We are presently collecting and evaluating similar data on radionucleide releases with respect to ARARs that have been developed at FEMP. Data available at this time indicate that these glasses can meet the required release limits for ^{99}Tc, ^{230}Th, ^{232}Th, ^{235}U, and ^{238}U. In terms of the overall leach resistance of the glass waste form it is useful to examine the release of major glass matrix components into solution under more aggressive conditions than those of the TCLP test. The PCT (2) that was developed for the high-level waste vitrification program is useful in this respect since there already exists a large database to provide a benchmark for comparison. The PCT procedure uses a higher temperature (90°C vs. 22°C), a longer time period (at least 7 days vs. 18 hrs), and a larger ratio of glass surface area to the volume of leachant (2000 m^{-1} (i.e. 10 g of 75-150μm powder in 100 ml of leachant) vs. about 20 m^{-1} (i.e. 100 g of material passing 3/8" sieve in 2000 ml of leachant)) than does the TCLP procedure. Figure 4 compares the average (over 7 days) normalized leach rates obtained using the PCT procedure for typical glasses prepared from FEMP wastes including Pit 5 sludge, soils, and fly ash. For comparison, the performance of the present standard glass for high-level waste acceptance (Savannah River Laboratory Environmental Assessment (SRL-EA) glass (10)) is also shown. Thus, it is possible to produce high-waste loading, processable glasses from FEMP low-level and mixed wastes that would meet the leach resistance requirements for disposal of high-level nuclear waste glasses. Furthermore, as outlined above, there is good evidence that this waste form option would be considerably less expensive than cement stabilization.

Several of these formulations have been tested using actual FEMP wastes in a 10 kg/day Duramelter vitrification system at VSL to obtain processing information. This system has been operated for six months using high-fluoride feeds. The off-gas system is able to remove fluorides from the off gas stream to emission standards and 100% recycle of the off-gas scrubber sludge to the melter feed has been demonstrated. We are presently evaluating off-gas data on emission of other contaminants of concern with respect to regulatory limits that may apply at FEMP; the initial data are very encouraging. The glass produced in these tests also passes the TCLP leach test.

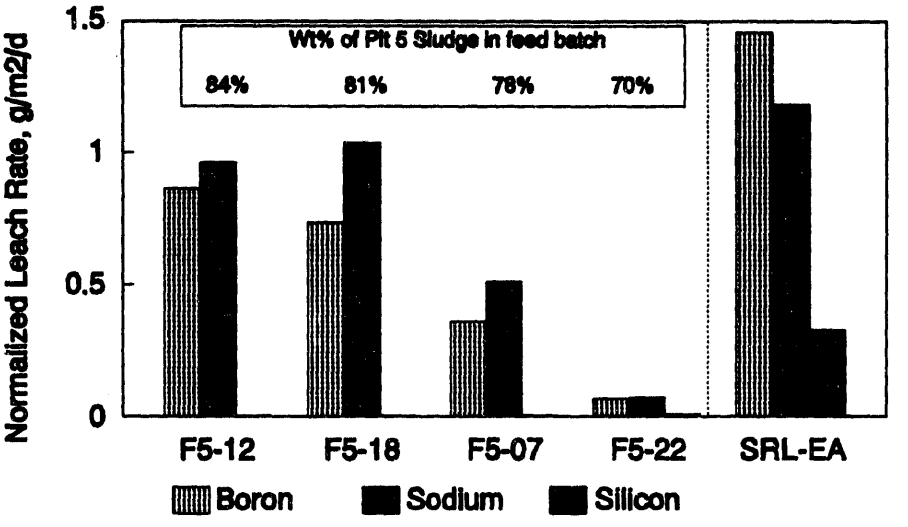

Figure 4. Comparison of PCT leach test results for Fernald glasses (F5-12, F5-18, F5-07, F5-22) with the Savannah River Laboratory high-level waste standard glass (SRL-EA). Leach rates for silicon are not visible for F5-12, F5-18, and F5-07 since all are below 0.004 $g^{-2}d^{-1}$.

The larger-scale, 100 kg/day Duramelter system installed at VSL has been operated for about seven weeks with non-fluoride surrogate feeds for general system tests; approximately 700 gallons of slurry feed have been processed through that system. Tests have included complete draining and restarting of the system. Corrosion checks after draining revealed no degradation of the electrodes or refractories. Preparations for radioactive operations include installation into the present interim off-gas system of the proprietary scrubber unit for fluoride capture and recycle, completion of system tests, and finalization of operating procedures. Our present test data already confirm that glass production rates of well in excess of the nominal 100 kg/day rate are achievable with this unit.

Design, procurement, and off-site construction of the 300 kg/day Duramelter vitrification system has been completed and the unit and some support systems have been delivered to the FEMP Plant 9 facility. Off-gas system components are now in the final phases of construction. Start-up of this on-site system is scheduled for May 1993. One month of start-up tests using non-radioactive feeds will be conducted under the Phase I contract.

Laboratory soil washing studies at LESC have resulted in the development of a viable system configuration that uses a combination of physical and chemical processes to achieve decontamination levels of below 35 pCi/g. Up to 80% volume reductions are obtained while producing a contaminant-enriched fraction that is depleted in calcium and enriched in silicon. Over 1700 kg of FEMP soil have been processed in these lab tests which also made use of an integrated GTS Duratek ion exchange water treatment system. About 350 kg of soil wash concentrates have been shipped to VSL for vitrification studies. Construction of the on-site TRUclean soil washing system is in progress with delivery and start-up planned for mid and late April 1993, respectively. Samples to determine the performance of the water treatment system will be generated and spent ion exchange media will be used for lab tests on regeneration and vitrification. The on-site water treatment system was delivered to the FEMP Plant 9 Facility in mid-March, 1993.

CONCLUSIONS

The potential benefits of an integrated, multiple-technology, blended-waste-stream treatment system for a site such as FEMP have been discussed. We have demonstrated that glass-based waste forms can be designed for low-level and mixed wastes that show excellent leach resistance, are processable using improved JHCM technology, and can achieve very high waste loadings. Furthermore, the very large volume reductions that have been demonstrated make vitrification a very much more economical option than cement stabilization particularly when life-cycle costs are considered. The synergisms possible between appropriately selected and optimized system components also serve to further increase waste loading, decrease additive requirements, and improve volume reductions. Many of the general MAWS concepts are applicable in a variety of alternative system configurations to suit available waste stream combinations characteristic of any given site. Finally, on-site demonstration, testing, and evaluation of the system will be performed at the FEMP site beginning in mid-1993. More detailed data on system performance should become available after that time.

ACKNOWLEDGEMENTS - As mentioned in the introduction, many institutions, and talented individuals too numerous to mention, have contributed to both the inception and the success of the MAWS program thus far. Credit is due to all involved for a very effective collaborative effort on a very aggressive schedule. This work is supported by The United States Department of Energy, Office of Environmental Restoration, and Office of Technology Development.

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