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—Waste Reduction and Minimization
—Prototype Licensing Applications

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VOLUME III

WASTE CHARACTERIZATION

WASTE REDUCTION AND MINIMIZATION

PROTOTYPE LICENSING APPLICATIONS WORKSHOP

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LOW-LEVEL WASTE MANAGEMENT
CONFERENCE

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WASTE CHARACTERIZATION

ISSUES IN LOW-LEVEL RADIOACTIVE WASTE CHARACTERIZATION

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INTRODUCTION

Central to the development of low-level radioactive waste (LLW) disposal facilities is the need to fully characterize the material being placed in the facilities. Characterizing the LLW for a particular facility is the first step in determining the type of facility to use, the appropriateness of the site selected for the facility, and determining compliance with State and Federal regulations. Yet some aspects of waste characterization are not known as well as the characterization of the selected site and the characterization of the facility. The main objectives for characterizing the waste that is to be placed in LLW disposal facilities are:

1. To determine the appropriate facility capacity and design.
2. To perform a safety assessment of the disposal facility and waste, both during operations and after the facility is closed.
3. To determine compliance with appropriate state and federal regulations, such as 10 CFR 61.[1]

In general, the data that are required in characterizing LLW are:

1. Annual volumes and total facility lifetime volumes.
2. Radionuclide concentrations and inventories.
3. Physical and chemical characteristics of the waste form, and package.

VOLUME PROJECTIONS

Determination of LLW volume projections over the 20- or 30-year lifetime of a facility is especially challenging at the present time because of the recent reductions in volume generated by commercial nuclear power plants. Figures 1 and 2 show the average annual volume of LLW generated per reactor unit for PWR's and BWR's.[2] Reductions of over a factor of three have occurred since 1980. It is also challenged by the potential impacts of present and future below regulatory concern (BRC) regulations and by the timing and magnitude of nuclear power plant decommissioning wastes. For example, as seen in Table I, the nuclear power industry petition for BRC disposal would involve over 1 x 10^6 ft^3 of LLW annually.[3] Low-level waste disposal volumes could decrease by a significant fraction of that amount with a negligible reduction in total activity disposed.

Low-level waste disposal volumes are also used to develop costs and disposal fees as well as input for safety performance assessments and the determination of appropriate operational procedures to be conducted by

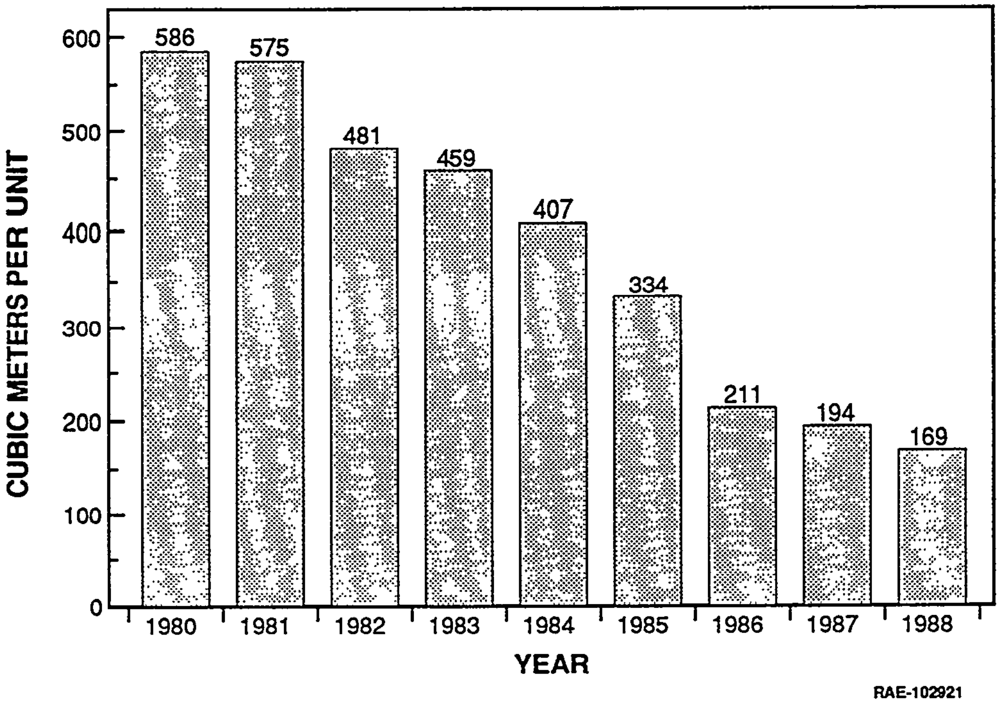

FIGURE 1. LOW-LEVEL RADIOACTIVE WASTE PER UNIT AT U.S. PRESSURIZED WATER REACTORS.

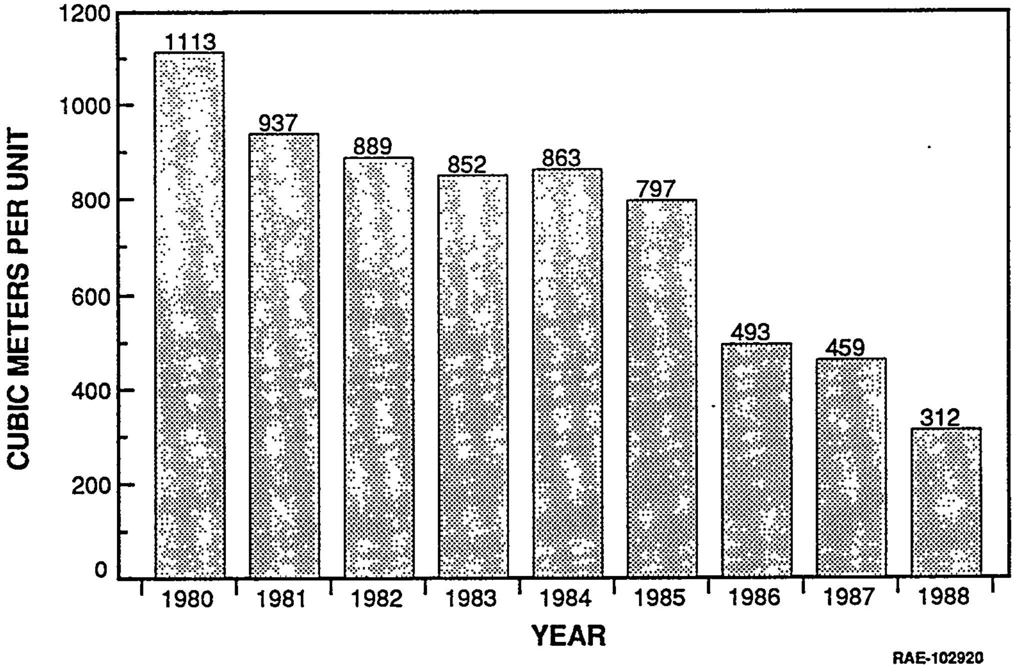

FIGURE 2. LOW-LEVEL RADIOACTIVE WASTE PER UNIT AT U.S. BOILING WATER REACTORS.

TABLE I

BRC WASTE VOLUME AND CURIE TOTALS FOR NUCLEAR INDUSTRY

Waste Type	Annual Volume (ft^3/yr x 1000)	Annual Curies (Ci/yr)
DAW	617	10.36
Oil	50	0.12
Soil and Water Treatment Sludges	51	0.02
Resins	736	10.62

facility workers. Because of the extensive data base developed by the Department of Energy and efforts by compacts and host states, annual volumes for past years and projections for future near-term years have been made, and applied to essentially every compact and host state. From the data base it is evident that disposal volumes can vary from year to year. This presents a potential problem for facility operators, particularly for states or compacts with relatively small annual disposal volumes because staffing needs and disposal costs may change greatly from year to year. Since some states require that disposal fees be based upon costs, and the annual costs may vary significantly due to variation in the volumes and activities disposed setting appropriate fees may be difficult and may need to be adjusted retroactively after the conclusion of each year.

RADIONUCLIDE CONCENTRATIONS AND INVENTORIES

Radionuclide Inventories and Concentrations are particularly important for the facility performance assessments, not only for long term performance after closure, but for determining the appropriate operations procedures and estimating worker exposures, and evaluating the impacts of potential accidents. Manifests on low-level waste shipments to disposal facilities presently contain the quantities concentrations of critical nuclides required for the waste classification. Many of these nuclides are not measured directly but are inferred from quantities of gamma emitting nuclides that are easier to measure. Thus, many waste inventories have the same relative concentrations among many nuclides. Often the generic nuclide inventory and concentrations develop by the Nuclear Regulatory Commission have been used to characterize some facility wastes. Table II contains scaling factors typical of those used in the nuclear power industry for estimating concentrations of nuclides that are difficult to measure. Also given are scaling factors from the NRC's GEIS supporting 10 CFR 61.[4]

With the development of the technical basis for the NRC's regulation (10 CFR 61) and EPA's regulations (40 CFR 193) extensive effort was made by both government agencies and by industry to improve the estimates of radionuclide concentration and inventories. Efforts were made to estimate a large number of nuclides including the hard-to-measure nuclides and the concentration means and statistical distributions were determined and analyzed. Generic performance assessments were performed that identified the critical importance of the long-lived mobile nuclides: C-14, Tc-99, I-129, and Np-237. The mobile nuclide H-3 was also identified to be important in some performance assessments.

PHYSICAL AND CHEMICAL CHARACTERISTICS OF LOW-LEVEL WASTE

This category is probably least understood in terms of quantified parameters that are needed for performance assessments. Physical and chemical characteristics are important in determining nuclide leach rates, the potential for the degradation of the waste form, waste package and disposal facility, and the prediction of the time dependance and magnitude of subsidence. Nuclide leach rates have been characterized for many solidified waste forms, however, the change in leach rate as the waste form degrades has been poorly characterized in general for waste forms that have degraded or for wastes that have not been subjected to a specific treatment and solidification process such as dry active waste, leach rates have not been

TABLE II

SCALING FACTORS FOR DAW

Nuclide Pair	Recent Industry Scaling Factor	NRC DEIS Scaling Factor
H-3/Co-60	0.01	0.026
C-14/Co-60	8.2E-3	1.0E-3
Fe-55/Co-60	0.514	0.517
Ni-63/Co-60	0.169	0.191
Sr-90/Co-60	8.5E-3	1.9E-3
Tc-99/Co-60	1.4E-4	8.19E-6
I-129/Co-60	9.83E-8	2.42E-5
Pu-239/Co-60	2.7E-4	4.8E-4
Pu-238/Pu-239	1.22	1.09
Pu-241/Pu-239	106.00	43.7
Am-241/Pu-239	0.57	0.72
Cm-244/Pu-239	0.48	0.47

characterized very well and usually equivalent soil equilibrium distribution coefficients (K_d) are used to estimate them. Table III contains approximate leach fractions, proportional to the inverse of retardation coefficients for waste leaching used by EPA.[5] In contrast, leach rates for solidified waste forms range from 10^{-5} to 5×10^{-4} yr^{-1}.

SUMMARY OF EARLY PROBLEMS

Early data bases contained relatively accurate volumes, although densities were usually not specified; thus, the degree of consolidation was very difficult to estimate from early data bases. The early data bases generally contained the total curies disposed and indication of the quantities of special nuclear material, mixed fission products, mixed activation products, or medical wastes. Often the specification of total curies ignored the identification of the activity of many important nuclides who dominated the potential health impact even though they represented less than 1 percent of the total impact. Commercial nuclear power plants would often just characterize their wastes as either dry active wastes or wet wastes.

All of the critical nuclides are relatively hard to measure and additional efforts have been undertaken to obtain more accurate and more representative concentrations for all LLW streams and to improve the relationship of the concentrations of these nuclides with other easy to measure nuclides. Other parameters whose values have been improved are the nuclide dose factors for ingestion, inhalation and internal gamma exposures, and the uptake of these nuclides through the food chain.

Briefly then, an examination of previous work on characterizing LAW revealed that:

1. Some waste streams were poorly defined.
2. The concentration and inventory estimates for many nuclides were inaccurate and for some nuclides were not even provided.
3. Conservatisms were applied for many hard-to-measure nuclides so that when nuclide concentrations were below detectable levels and "less than" values were reported, these less than values were often reported as actual concentrations; thus, greatly overestimating the inventory of these nuclides and adversely influencing the results of performance assessments.
4. Much of the data were too sparse to allow appropriate generalizations
5. Documentation was missing or errors occurred.
6. In general, the quality assurance and quality control on the original data was insufficient.
7. Volumes and activities varied significantly from year to year and generator to generator.
8. Generic data have been used for very facility specific analyses.

TABLE III

APPROXIMATE LEACH FRACTION FOR DEGRADED WASTE FORM

Nuclide	Approximate Leach Fraction (yr^{-1})
H-3	9.46E-01
C-14	9.46E-01
Fe-55	3.50E-03
Ni-59	3.50E-03
Co-60	3.50E-03
Ni-63	3.50E-03
Sr-90	5.81E-03
Nb-94	2.50E-03
Tc-99	2.60E-01
Ru-106	2.50E-03
Sb-125	3.88E-03
I-129	5.52E-02
Cs-134	1.75E-03
Cs-135	1.75E-03
Cs-137	1.75E-03
Ba-137m	1.75E-03
Eu-154	4.39E-05
Ti-208	2.92E-06
Po-210	7.97E-04
Pb-210	7.97E-04
Pb-212	2.92E-06
Bi-214	7.97E-04
Pb-214	7.97E-04
Ra-226	7.97E-04
Th-228	2.92E-06
Ac-228	7.97E-04
Ra-228	7.97E-04
Th-232	2.92E-06
U-234	2.34E-04
U-235	2.34E-04
Np-237	3.39E-02
U-238	2.34E-04

NEEDS FOR WASTE CHARACTERIZATION

In order to assemble an appropriate data base for the characterization of low-level waste in a specific compact or state, the following items should be addressed:

1. Quality assurance of the date base.
2. Improved concentration estimates for key nuclides.
3. Compact and site specific nuclide data.
4. Present volumes and future volume trends for each nuclear plant.
5. An appropriate method for treating nuclide concentrations reported as "less than" the lower limit of detection.

The existing data bases or new data bases should receive a thorough quality assurance and quality control evaluation. Specifically, were transcribing errors made in developing the data base? Is the supporting documentation sufficient? Were computational errors made in determining nuclide concentrations and quantities? Were split samples, spiked samples, and blank samples sent for laboratory analysis along with the main samples? Were the proper procedures used in the laboratory analysis? Were the original samples obtained correctly and are they representative of the entire waste stream? Were there any unusual occurrences that biased the data base in an inappropriate manner?

An additional need is the improved determination of concentrations for key nuclides. Because H-3, C-14, Tc-99, I-129, and Np-237 are difficult to measure, it is appropriate to use scaling factors with easy-to-measure nuclides. These scaling factors have already been determined. Are they correct? Or, have errors occurred in developing the scaling factors? Are the scaling factors being used correctly by the individual waste generators? Are there some waste streams where a generic factor is being used that may underestimate or overestimate the actual concentration and quantity of a critical nuclide? While a conservative overestimate of the concentration or activity of a critical nuclide helps ensure a conservative safety analysis, incorrect actions may be taken and unnecessary costs may be incurred as a result of the overly-conservative estimates. For example, it is presently generally regarded that Iodine-129 concentrations and inventories in DAW have been overestimated by more than 2 orders of magnitude. Performance assessments, that have been conducted using incorrect values, indicate that the long-lived mobile nuclide I-129 dominates the calculated doses and that engineered barriers such as an improved waste form, waste package, or concrete vault, do little to reduce the magnitude of the peak dose. Reducing the I-129 concentration by 2 or 3 orders of magnitude may greatly alter the results of performance assessments.

Compact-specific nuclide data is an additional need that must be met. In the absence of a compact-specific nuclide data base the generic nuclide concentrations developed by the NRC or EPA are often used and once again may give misleading results in performance assessments.

Associated with the development of an appropriate nuclide data base is the need for developing an appropriate way to handle nuclides that are reported as "less than" quantities.

Finally, careful consideration of the annual volumes and trends in volumes per nuclear plant and major industrial/institutional generator must be developed. Volume trends have been sharply downward in recent years and may continue to decrease. On the other hand, if a state or compact provides no incentive for volume reduction, this recent trend may reverse itself and annual volumes may increase.

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IMPROVED SAMPLING AND ANALYTICAL TECHNIQUES FOR CHARACTERIZATION OF VERY-LOW-LEVEL RADWASTE MATERIALS FROM COMMERCIAL NUCLEAR POWER STATIONS

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ABSTRACT

This paper summarizes the unique sampling methods that were utilized in a recently completed project sponsored by the Electric Power Research Institute (EPRI) to perform accurate and precise radiological characterizations of several very-low-level radwaste materials from commercial nuclear power stations. The waste types characterized during this project included dry active waste (DAW), oil, secondary-side ion exchange resin, and soil. Special precautions were taken to insure representative sampling of the DAW. This involved the initial direct, quantitative gamma spectrometric analyses of bulk quantities (208-liter drums) of DAW utilizing a specially constructed barrel scanner employing a collimated intrinsic germanium detector assembly. Subsamples of the DAW for destructive radiochemical analyses of the difficult-to-measure 10CFR61 radionuclides were then selected which had the same isotopic composition (to within ± 25%) as that measured for the entire drum of DAW. The techniques for accomplishing this sampling are described. Oil samples were collected from the top, middle and bottom sections of 208-liter drums for radiochemical analyses. These samples were composited to represent the entire drum of oil. The accuracy of this type of sampling was evaluated by comparisons with direct, quantitative assays of a number of the drums using the barrel scanning gamma-ray spectrometer. The accuracy of sampling drums of spent secondary-side ion exchange resin was evaluated by comparing the radionuclide contents of grab samples taken from the tops of the drums with direct assays performed with the barrel scanner. The results of these sampling evaluations indicated that the sampling methods used were generally adequate for providing a reasonably representative subsample from bulk quantities of DAW, oil, and resin. The study also identified a number of potential pitfalls in sampling of these materials.

1. INTRODUCTION

Since the implementation of 10CFR61 (1), the nuclear power industry has been faced with the challenge of conducting detailed radionuclide analyses of a wide variety of radwaste materials. Obtaining representative samples of these materials for analyses has presented a number of complex problems, and reliable sampling remains one of the major uncertainties in the 10CFR61 compliance program (2). The sampling problems are most acute for the very-high and very-low-activity types of radwastes. For the very-high-activity samples (e.g., primary resins, primary filters, activated metals, etc.), the high gamma dose rates associated with these materials limit the size of the sample aliquot that can be conveniently collected, handled, and analyzed. For non-homogeneous radwaste materials, such a small sample (usually a few milligrams) is often not representative of the whole quantity of waste (often 100's to 1000's of kilograms). For the very-low-activity radwastes, just the opposite sampling problem frequently occurs, and very large samples are required to detect the low concentrations of radionuclides. Such large samples often tax the analytical methods and measurement errors are introduced. Also, the analytical results are so close to the detection limit that false-positive values are often reported.

Recently, the Electric Power Research Institute (EPRI) conducted an extensive research program aimed at generating the technical bases for developing a special rule-making petition to the Nuclear Regulatory Commission (NRC). This petition would seek to exempt certain waste streams from commercial nuclear power stations as "below regulatory concern" (BRC) waste, if the activity of the waste was below a specified, yet-to-be-determined, safe level. As part of this research program, Battelle, Pacific Northwest Laboratories conducted an extensive radiological characterization of four major solid waste streams considered to be prime candidates for BRC exemption; dry active waste (DAW), oil, soil, and secondary-side ion exchange resin (3). An onsite collection task was conducted by another subcontractor which provided large quantities of these slightly contaminated materials for 10CFR61 radionuclide analyses. These very-low-activity materials presented special sampling and analysis problems, and several unique measurement techniques were developed to insure representative, accurate, and reliable radioanalytical results. These data were then utilized for assessing the true variability in the radionuclide distributions for these wastes. This paper describes the special sampling and analysis methods utilized in this program.

2. SCOPE OF PROJECT

The EPRI characterization project addressed the requirements for adequately determining the radiological properties of potential BRC waste streams. The waste streams selected for detailed radiological characterization were DAW, oil, soil, and secondary ion exchange resin. The DAW makes up, by far, the largest volume fraction of these waste streams.

The radiological properties addressed in this characterization included:

- The identification of the radionuclides present.
- The average concentration of the radionuclides.
- The distribution and variability of the nuclide composition or quantities.

Ten plants, including six PWRs and four BWRs, representing 12 reactor units were selected for this study. The ten initial plants were selected for sampling of DAW and the other available BRC waste types on the basis of fuel performance parameters. Because oil, soil, and secondary resin wastes were not always available at the initial ten plants, an additional three PWRs and three BWRs were included in the program to augment the sample collection.

The basic approach in the plant selection process was to select a few plants which had relatively extensive quantities of exposed fuel in the primary system and a few plants with minimal fuel failures. The extent of failed fuel is directly proportional to the level of difficult-to-measure radioisotopes, such as the transuranic and fission product nuclides, in nuclear plant wastes. This approach ensured that the entire range of failed fuel conditions (and range in radionuclide composition of plant wastes) in operating plants was accommodated in the sampling program.

The radionuclides that were measured in this program included all detectible gamma-emitters (including ^{60}Co and ^{137}Cs), ^{14}C, ^{55}Fe, ^{63}Ni, ^{90}Sr, ^{94}Nb, ^{129}I, ^{238}Pu, and ^{239,240}Pu. All of the samples were measured for the gamma-emitters, ^{90}Sr, ^{238}Pu, and ^{239,240}Pu, while 10% of the samples were analyzed for ^{14}C, ^{55}Fe, ^{63}Ni, and ^{129}I. Tritium and ^{99}Tc were not analyzed because the industry-wide 10CFR61 data base was felt to be sufficient. Also, a performance assessment for a LLW shallow land burial site indicated their concentrations would be orders of magnitude below any level of significance in the dose assessments. Nickel-59, ^{241}Am, ^{241}Pu, and ^{242,244}Cm were also not measured because the ^{59}Ni/^{63}Ni, Am/Pu, ^{241}Pu/^{238}Pu, and Cm/Pu scaling factors for all types of reactor wastes are reasonably constant and their concentrations can be reliably estimated using the industry scaling factors. Thus, all of the 10CFR61 radionuclides were either directly measured or estimated from reliable waste-stream specific or generic scaling factors.

To help verify the representativeness of the sampling and analysis of the indicated radwaste materials, direct assay techniques were developed for determining the spatial distribution and concentrations of the radionuclide contents of entire 208-liter drums of DAW, oil, and resin. Comparing these direct, bulk assays with grab samples of the radwaste materials helped define the variability of the sampling.

3. SAMPLING AND ANALYTICAL STRATEGIES

Each type of radwaste material presented its own peculiar sampling problems. This section discusses the sampling and analytical strategies used in this project to provide representative assays of the radionuclide contents of the various wastes.

3.1 Dry Active Waste (DAW)

DAW is the most difficult radwaste material to sample and analyze. The DAW waste stream typically contains non-halogenated plastic, paper, wood scrap, clothing, packing materials, lagging, light metals, plastic sheet, rubber gloves and boots, and other miscellaneous items. The radionuclide contamination of these materials is extremely patchly, not only in terms of concentration, but also in isotopic composition. It is therefore very difficult to extract a grab sample from a large batch of DAW that is representative of the batch. Usually, most of the surface area of a contaminated item is relatively free of radioactive material, and most of the contamination is present as "hot spots" of localized activity. When sampling such items, especially for very low activity DAW, large quantities of essentially non-radioactive material are included with the contaminated areas, and the analytical task is complicated by the large volumes of waste being analyzed. To circumvent this problem, it has been the practice in the nuclear power industry to obtain highly contaminated filter paper smears of residual contamination from floors or equipment and assume that this radionuclide composition and concentration is representative of DAW. This non-representative sampling has a large potential for error.

As a requirement for BRC rule-making petitions, the NRC has stipulated that the proposed waste streams be adequately characterized using actual samples of the waste material (4). Therefore, the radionuclide characterization program in support of the EPRI BRC rule-making petition program required that accurate, reliable assays of very-low-activity DAW be conducted on actual samples of slightly contaminated material. The sample inhomogeneity problems for DAW were greatly minimized during the EPRI BRC radiological characterization program by applying the following sampling and analysis strategies.

The strategy for conducting these representative measurements first involved the direct quantitative gamma-spectrometric analysis of 208-liter drums of semi-compacted DAW collected at the 10 nuclear power stations. The drums contained DAW that had been sorted and segregated at each reactor site into nine different surface contamination categories, ranging from <1000 dpm/100 cm^2 to >62,5000 dpm/100 cm^2. The DAW sorting and segregation was conducted by National Nuclear Corporation personnel using very sensitive, large-area, hand-held survey meters.

After quantitatively determining the average concentrations of the gamma-emitting radionuclides, including ^{60}Co and ^{137}Cs, on a mass (μCi/g) basis, for the entire drum of DAW, subsamples of the DAW for radiochemical analyses were collected from the drummed waste which had the same $^{60}Co/^{137}Cs$ activity ratio (within ±25%) as that determined for the entire drum. The ^{60}Co and ^{137}Cs were considered to be representative of the activation and fission product/TRU radionuclides, respectively. In this way, the subsamples collected for radiochemical analysis of the difficult-to-measure radionuclides were representative of the average radionuclide composition of the entire drum. The average concentrations of the non-gamma-emitting radionuclides for the entire drum of DAW could then be determined after the radiochemical analysis by scaling-up, using ^{60}Co and ^{137}Cs activity ratios measured for the drum and in the subsamples.

3.1.1 Direct Assay of Bulk DAW by Barrel Counting

The barrel-counting direct measurement system used in this work is schematically illustrated in Figure 1. A lead-collimated, shielded IG detector is mounted on a moveable platform which vertically scans a 208-liter drum from top to bottom. The drum is mounted on a turntable which rotates

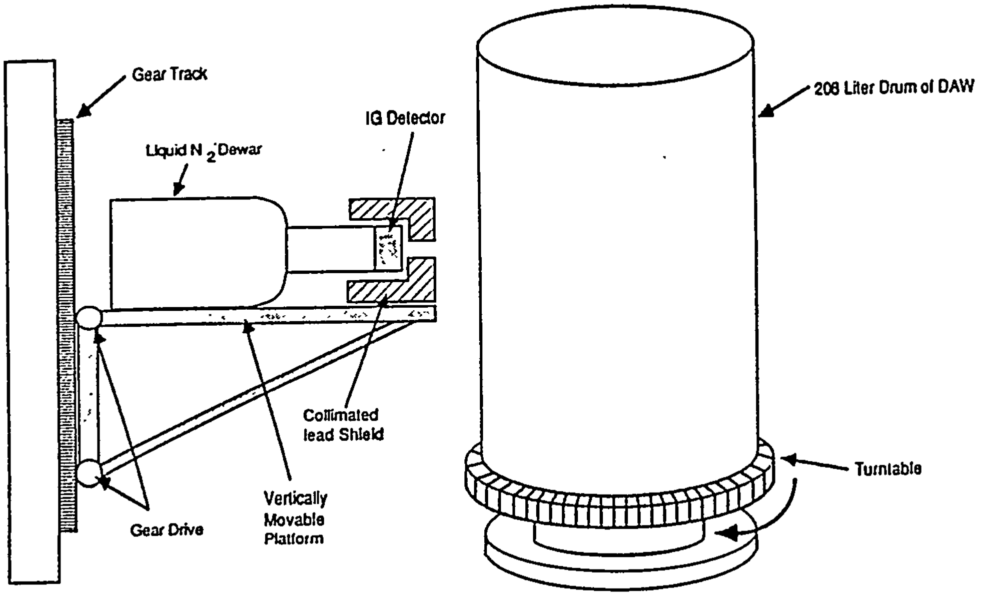

Figure 1. Schematic Diagram of a 208-Liter Barrel Counter for Direct Isotopic Measurement of Sub-BRC Levels of Gamma Activity in Bulk DAW

the drum at approximately 30 revolutions per minute during the vertical scanning. The vertical gamma scanning is normally performed in eleven 7.6 cm segments and each segment count is summed to provide both total gamma activity and specific activity, as well as individual isotopic activity. The vertical distribution of activity in the drum can also be determined. This information is useful in the event that some portion of the waste in the drum contains a highly unusual radionuclide composition and would not be desirable as a subsample for radiochemical determination of the difficult-to-measure radionuclides.

This counting system contains a relatively large IG detector (about 30% efficient) which is shielded by surrounding it with 4 to 5 cm of lead. The lead shield is collimated at the active end of the diode with an opening which may be varied from a 1-cm diameter hole to a 2.5-cm wide slit, depending upon the activity of the waste. For the BRC monitoring of DAW, the 2.5-cm wide slit was used to provide maximum counting efficiency. This system also contains two half-cylinders of $^{10}BF_3$ neutron detectors which surround the drum. These detectors measure neutrons emitted by transuranic (TRU) isotopes in the waste and can be used to directly measure the concentrations of Pu, Am, and Cm in the waste if their concentrations are above about 1 nCi/g. However, none of the BRC wastes measured in this project had TRU concentrations this high, and the neutron counting data was not utilized since Pu was radiochemically measured.

Because this type of gamma counting system vertically scans the drum as it rotates, the radiation incident on the detector approximates that from a "homogenized" sample. The net effect is that both sensitivity and counting geometry variability are improved.

The most critical variable associated with barrel counting is the density of the waste material, and appropriate corrections in counting efficiency must be made for variable densities. A series of calibrations were conducted, as described in Reference 3, which determined the counting efficiencies for both homogeneously distributed and point-source conditions. The calibration curves for the homogeneously distributed source as a function of sample density are shown in Figure 2.

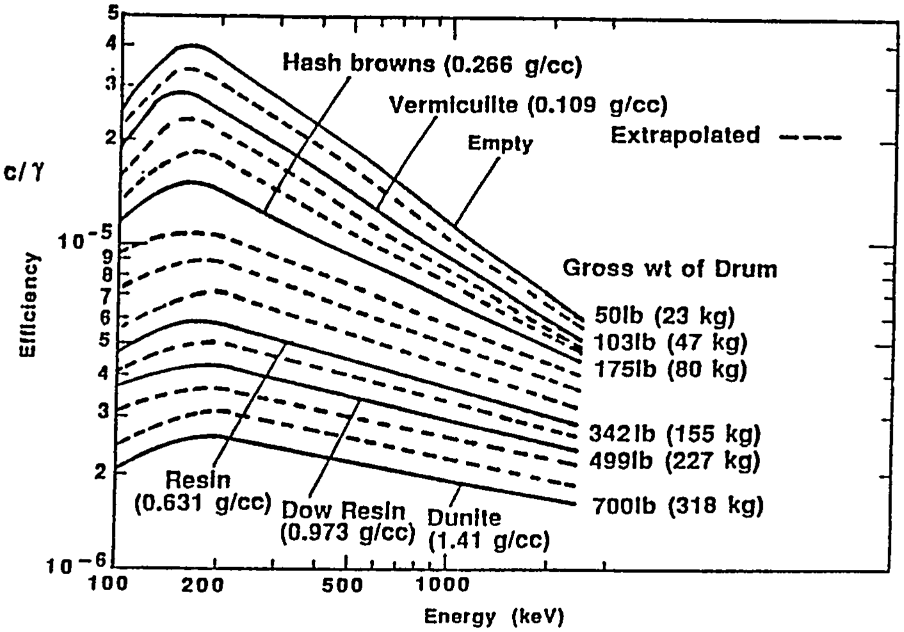

Figure 2. 208-Liter Drum Calibration Curves (Homogeneous Distribution)

It was determined that for relatively low sample densities (e.g. uncompacted DAW) the semi-point-source calibration standard produced counting efficiency curves that were within ± 10% of those provided by the homogeneously distributed standard. Thus, it was assured that the efficiency curves used for the homogeneously distributed activity simulating semi-compacted DAW will be valid to within ± 10% for a point source of activity (simulating a hot-spot or particle) located within the drum. It is possible to identify the approximate vertical location of hot-spots or particles within the drum during the vertical scanning.

The reliability detectable activity (RDA) achieved by the barrel counting, as defined by Thomas et al. (5), for a typical density of slightly compacted DAW of 0.27 g/cc was 0.063 μCi, or 1.1E - 6 μCi/g for a full drum for a 4400 second counting interval.

A total of 102 208-liter drums of DAW were directly assayed at Battelle, Pacific Northwest Laboratories by gamma-ray spectrometry. These included 60 drums from six PWR stations and 42 drums from four BWR stations. The barrel counter was set up in a low-background building free of any radioactive sources. The drums of DAW were weighed, and each was counted for a total of 4400 seconds by scanning the drum vertically in eleven 7.6-cm wide segments as the drum rotated on the turntable at 30 rpm. The eleven discrete segment counts were summed to provide a total count rate for the whole drum. The RAYGUN gamma-ray analysis code was utilized to identify and quantify the radionuclide concentrations in the waste (6). The average concentration of each detectable radionuclide in the waste was reported in units of μCi/g of DAW. In addition, the vertical variability of the radionuclide composition of the waste in each drum could be determined after data reduction of each segment count. This provided an assessment of the range in radionuclide composition within each drum, and also assisted the subsampling of DAW in each drum for radiochemical analyses to insure representativeness of the subsamples.

3.1.2 Subsampling DAW for Radiochemical Analyses

The overall approach for obtaining a representative sample of DAW for radiochemical analysis (hereafter referred to as the subsample) from a 208-liter barrel was to collect material from the barrel that had approximately the same ^{60}Co/^{137}Cs ratio (within ± 25%) as the average value for the whole barrel, and contained, where possible, at least 10% of the total ^{60}Co and ^{137}Cs activity of the drum. The radionuclides ^{60}Co and ^{137}Cs were selected to confirm sample representativeness because of their relatively higher activity levels and easily measurable gamma-rays, and because they generally represented the activation and fission/TRU products, respectively. By obtaining at least 10% each of the total ^{60}Co and ^{137}Cs present in a barrel, a sufficient amount of the other activation and fission products could be obtained for their accurate determination. The radionuclides measured in these subsamples included ^{14}C, ^{55}Fe, ^{63}Ni, ^{90}Sr, ^{129}I, ^{238}Pu, and ^{239,240}Pu. Because of the anticipated low ^{129}I activity levels, separate aliquots were removed from the highest activity subsample of each plant for additional ^{129}I analysis by highly sensitive mass spectrometry.

Once the barrels had been selected from a power plant for subsampling, the gamma scans for each of the eleven vertical segments of a barrel (determined from the barrel counting) were analyzed for their ^{60}Co and ^{137}Cs contents and their ^{60}Co/^{137}Cs ratio. This vertical profile of each barrel aided in locating the best areas within the barrel to sample for achieving the desired ^{60}Co/^{137}Cs ratio which matched the average ratio for the entire drum of DAW.

Using a Geiger-Muller counter, pieces of waste that contained elevated radioactivity levels were removed and placed into 250 ml plastic jars and gamma-counted on GeLi detectors to determine their ^{60}Co and ^{137}Cs contents. The frisking with the Geiger-Muller counter also allowed for the reduction in the volume of inert waste subsampled from the barrels. When possible, small areas of relatively high contamination levels were cut out of larger articles to reduce the volume of a subsample.

The 250-ml plastic jars containing the subsamples from a barrel were then counted on a GeLi gamma-ray spectrometer to determine their ^{60}Co and ^{137}Cs concentrations. Several of the 250-ml jars were then chosen for blending of the selected DAW pieces to obtain a final subsample with the desired ^{60}Co/^{137}Cs ratio and, where possible, contained greater than 10% of the total ^{60}Co and ^{137}Cs activity within a barrel. The contents of the selected jars were then shredded and mixed together to obtain a homogenized subsample. The homogenized subsample was finally placed into a 1-liter Marinelli beaker and gamma counted in this standard geometry to determine the final ^{60}Co and ^{137}Cs concentrations of the material used for the radiochemical analyses.

If the ^{60}Co/^{137}Cs ratio was not within ± 25% of the average ratio of the entire drum, other 250-ml jars were selected and added to the mixture to obtain the proper ^{60}Co/^{137}Cs ratio and radionuclide content. The unused waste was returned to the barrel and stored for possible later use. The final subsample was weighed and used for the radiochemical analyses.

3.1.3 Radiochemical Analysis

The analytical flow scheme used for the radiochemical analyses of the subsamples of DAW is shown in Figure 3. This scheme was typical of that used for the oil, soil, and resin samples with slight modification to accommodate the different matrices.

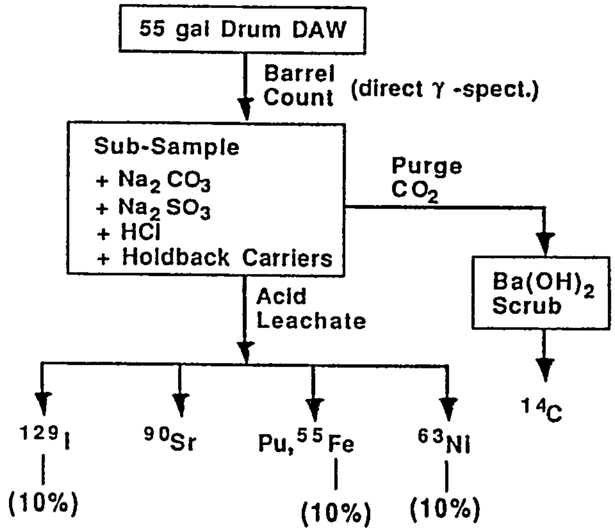

Figure 3. Flow Scheme for DAW Analyses

The subsample of weighed and gamma counted DAW was placed in a purging flask. The sequential analysis scheme started with ^{14}C, and 200 mg of Na_2CO_3 and 200 mg of $NaHSO_3$ were added and stirred into the shredded DAW. Then 1000 ml of 6 N hydrochloric acid was added, the flask was placed on a hot plate, and the sample was purged with CO_2-free air for 3 hours to sweep out the ^{14}C as CO_2. The CO_2 was trapped in a series of $Ba(OH)_2$ scrubber solutions which contained a pH indicator to insure that the solutions never became acidified. After purging of the CO_2, the ^{14}C in the $Ba(OH)_2$ scrubber solution was separated as $BaCO_3$, purified and counted.

The residual DAW in the purging flask was transferred to 4-liter beakers and hot 6 N hydrochloric acid was added to cover the DAW. The mixture was boiled for 2 hours to leach the radionuclides from the shredded DAW. This was repeated twice and the acid leachate combined. The ^{60}Co and ^{137}Cs in the waste were used as internal tracers of the leaching efficiency by recounting the DAW subsample on a GeLi detector after the acid leaching.

The average leaching efficiency using 300-500 grams of DAW was about 85%, as determined by utilizing using the ^{60}Co and ^{137}Cs as internal yield tracers. The acid leachate was then divided into four aliquots for radiochemical analyses of ^{55}Fe, ^{63}Ni, ^{90}Sr, ^{129}I and Pu isotopes. Iron-55 and Pu were determined sequentially from the same aliquot. All of the subsamples were analyzed for ^{90}Sr and Pu, whereas 10% of the subsamples were analyzed for ^{55}Fe, ^{63}Ni and ^{129}I. As mentioned earlier, separate subsamples of shredded DAW were taken for ultra-sensitive ^{129}I by mass spectrometry.

3.1.4. Radionuclide Variability and Representative Sampling of DAW

To illustrate the problems of representative sampling of inhomogeneous DAW, an example is taken from the radiological characterization of several of the 102 drums of DAW analyzed by direct gamma spectrometry during the EPRI BRC program. Table 1 is a tabulation of the gamma-emitting radionuclide concentrations for drums of DAW from PWR Station D, averaged over the contents of the entire drum, as determined by direct assay using the barrel counter.

Table 1

Radionuclide Concentrations in 208-Liter Drums
of DAW by Direct Assay - PWR Station D

				Concentration - μCi/g				
Drum #	Drum wt (lbs)	DAW wt (kg)	Activity Category	^{58}Co	^{60}Cs	^{134}Cs	^{137}Cs	Total γ Act.
2	103.8	24.38	<1K	4.48E-5	1.66E-5	2.02E-5	2.34E-5	1.17E-5
3	90.0	18.14	<1K	2.61E-5	3.91E-5	1.17E-5	1.48E-5	9.44E-5
4	86.5	16.56	<1K	1.43E-5	1.37E-5	1.57E-5	4.26E-5	8.87E-5
5	104.0	24.99	<1K	2.32E-5	7.73E-5	1.11E-5	1.73E-5	1.39E-4
1	109.5	26.99	1-5K	7.97E-5	1.14E-5	3.76E-5	5.96E-5	2.44E-5
8	77.5	12.47	1-5K	5.60E-5	2.70E-5	1.88E-5	2.59E-5	1.53E-5
6	88.8	17.56	5-10K	2.00E-4	3.65E-4	1.45E-4	2.86E-4	1.09E-3
7	89.5	17.92	10.20K	4.40E-4	3.16E-4	1.96E-4	2.69E-4	1.42E-3
10	60.0	4.54	20-37K	3.65E-4	7.81E-4	3.38E-4	5.52E-4	2.23E-3
9	121.0	32.21	>62.5K	2.27E-3	8.85E-4	1.29E-3	1.67E-3	9.08E-3

Table 2 presents the percent abundance of the gamma-emitters for the DAW in the same group of drums, and illustrates the variability of the radionuclide composition from drum to drum.

Table 2

Percent Abundance of Gamma-Emitting
Radionuclides in 208-Liter Drums
of DAW - PWR Station D

Drum #	Activity Cat. (dmp/100 cm^2)	% of Total γ Activity					
		^{60}Co	^{58}Co	^{54}Mn	^{95}Nb	^{134}Cs	^{137}Cs
2	<1K	14.2	38.3	2.8	10.2	17.3	20.0
3	<1K	41.2	27.6	2.9	<6.1	12.4	10.8
4	<1K	15.4	16.1	2.7	<5.5	17.7	16.7
5	<1K	52.0	16.7	4.0	6.5	8.0	12.4
1	1-5K	46.7	32.7	4.8	8.6	15.0	24.4
8	1-5K	17.6	36.6	4.0	12.1	12.3	16.9
6	5-10K	33.5	18.3	3.4	5.8	13.3	26.2
7	10-20K	22.3	31.0	3.5	8.4	13.8	18.9
10	20-37.5K	35.0	16.4	3.1	4.4	15.1	24.8
9	>62.5K	32.0	12.5	2.8	8.8	18.2	23.6
	X	30.9	24.6	3.4	7.6	14.3	19.5
	σ	13.3	9.6	0.69	2.4	3.1	5.3

As shown in Figure 4, the vertical distribution of ^{60}Co, relative to ^{137}Cs, in six drums of DAW from PWR Station D varied by as much as a factor of 10 to 20 for several of the drums. Drum #9 was selected for this example because it contained the highest activity category of waste (>62,500 dpm/100cm^2) from this station, and the counting statistics for the direct assay and the DAW subsampling were very good.

As shown in Figure 4, the vertical distribution of the ^{60}Co/^{137}Cs ratio of the DAW in Drum #9 varied from about 0.2 to 2.2 as determined from the eleven segments of the barrel count, and the average ratio for the entire drum was

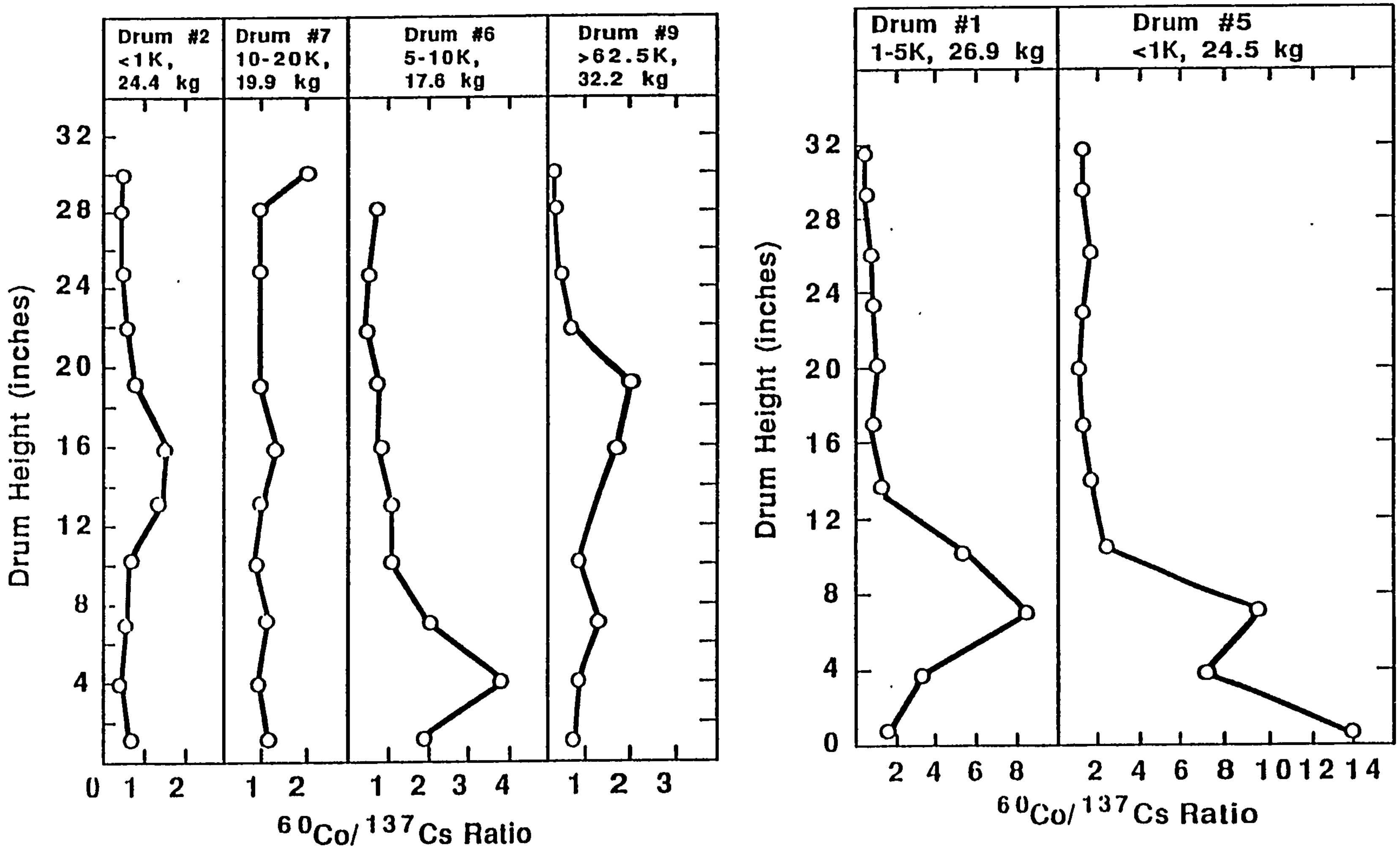

Figure 4. Typical Vertical Variability of the $^{60}Co/^{137}Cs$ Ratio in 208-Liter Drums. PWR Station D

0.53. During the subsampling of this drum for radiochemical analyses, 21 separate pieces of DAW material were removed from the drum, placed in standard 250-ml counting containers, and quantitatively analyzed on a GeLi gamma-ray spectrometer. The results of this subsampling, shown in Table 3, dramatically illustrate the extreme piece-by-piece variability of the isotopic composition of DAW in this drum. As Table 3 indicates, the ^{60}Co/^{137}Cs ratio for the 21 pieces of DAW subsampled from Drum #9 ranged from 0.164 to 59.8, a factor 3650. Also, the total activity on each piece of DAW varied by up to a factor of 200. Thus, it is clear that a true radiological characterization of a batch of DAW cannot be made by analyzing a single piece, or even several pieces of DAW from the batch.

Table 3

Subsampling of 208-Liter Drum of DAW for Blending Radionuclide Concentrations

Drum #9, >62.5K, PWR Station D

Sample	^{60}Co (dpm x 10^4)	^{137}Cs (dpm x 10^4)	^{60}Co/^{137}Cs
1	4.63	29.7	0.156
2	1.88	18.7	0.101
3	6.63	391	0.170
4	13.5	291	0.0464
5	2.63	160	0.0164
6	8.00	218	0.0367
7	7.00	36.2	0.193
8	1.13	7.82	0.144
9	0.25	1.79	0.140
10	12.3	4.25	2.89
11	0.38	8.93	0.0420
12	1.88	6.72	0.279
13	168	2.81	59.79
14	3.63	8.42	0.431
15	4.88	21.9	0.223
16	5.63	24.1	0.234
17	10.0	7.57	1.32
18	4.63	15.8	0.293
19	10.5	20.9	0.502
20	4.50	19.0	0.237
21	6.50	26.4	0.246

The objective of the DAW subsampling used in the EPRI BRC program was to provide a composite sample composed of pieces of DAW which, in combination, yielded the same ^{60}Co/^{137}Cs ratio (within ± 25%) of that measured for the entire drum of DAW as determined from the barrel count. This would provide a much more representative mix of activation products (represented by ^{60}Co) and fission/TRU products (represented by ^{137}Cs) in the composite sample than could be achieved by random grab sampling. The selection of appropriate subsamples of DAW to make up the composite sample having the same ^{60}Co/^{130}Cs ratio as the drum is illustrated in Table 4. Seven of the 21 DAW pieces having appropriate ^{60}Co and ^{137}Cs contents were combined to give a ^{60}Co/^{137}Cs ratio of 0.471, which compared favorably to a ratio for the entire drum of 0.53. This provided only an 11% difference in ratio between the composite DAW sample and the entire drum of DAW. Such successful blending of subsamples was accomplished for all of the 102 drums of DAW analyzed during this project.

Table 4

Blending of DAW Subsamples from Drum #9
to Match the ^{60}Co/^{137}Cs Ratio
of the Entire 208-Liter Drum of DAW

Sample	^{60}Co (dpm x 10^4)	^{137}Cs (dpm x 10^4)
10	12.3	4.25
12	1.88	6.72
17	10.0	7.57
19	10.5	20.9
16	5.63	24.1
20	4.50	19.0
21	6.50	26.4
	Σ 51.3	Σ 109

		% Diff.
Composite	^{60}Co/^{137}Cs = 0.471	
Barrel	^{60}Co/^{137}Cs = 0.530	11.3

An example of the blending of composite DAW samples for radiochemical analysis of the non-gamma emitting radionuclides for all of the DAW drums analyzed from PWR Station D is shown in Table 5.

Table 5

Subsampling of 208-Liter Drums of DAW for Radiochemical Analyses of Non-Gamma Emitting Radionuclides - PWR Station D

Drum #	Activity Category	Total Drum Count $^{60}Co/^{137}Cs$	Composite Sub-sample $^{60}Co/^{137}Cs$	% Diff.	Fraction of Total Drum Act. in Composite
3	<1K	2.64	2.84	7.6	0.128
4	<1K	0.32	0.30	6.3	0.0242
1	1-5K	1.92	2.25	17.2	0.167
8	1-5K	1.04	0.99	4.8	0.232
6	5-10K	1.28	1.22	4.7	0.0664
7	10-20K	1.17	1.00	14.5	0.103
9	>62K	0.53	0.47	11.3	0.0382

The percent difference in the $^{60}Co/^{137}Cs$ ratios for the composite DAW samples compared to the ratios for the entire drums ranged from 4.7% to 17.2%. The fraction of the total activity of each drum represented by the composite sample ranged from 0.038 to 0.232. These relatively high fractions of the total drum DAW activity were possible by cutting out the "hot spots" of contamination on the selected subsamples of DAW, thus eliminating a large volume of uncontaminated material.

The special sampling techniques developed during the EPRI BRC radiological characterization program were very effective in providing reliable measurements of the radionuclide distributions, composition, and variability for DAW. These methods could be utilized for essentially any radionuclide analyses of DAW materials.

3.2 Oil

Obtaining a representative sample of contaminated oil from 208-liter drums or other large containers for radionuclide analysis is more complicated than most people realize. This is because most contaminated oil contains fine particles of radioactive materials or entrained contaminated water which usually have much higher specific activities compared to the oil matrix. In addition, the particles and water settle to the bottom of the drum over time, creating a large vertical gradient in activity from the top to the bottom of the drum.

During the EPRI BRC project, the problems of sampling oil were investigated. Fifty-three drums of oil were sampled from eight plants to evaluate the concentrations of radioactive materials in spent oil. To evaluate sampling representativeness, 1- to 2-liter samples were collected from the top, middle, and bottom of each drum for a total of 159 samples. In addition, a number of grab samples were collected from several drums, sometimes in duplicate, to further characterize the radiological properties of the oil. A total of 127 oil samples were obtained from five PWRs and 62 samples from two BWRs were collected. In addition, 42 drums of oil from two stations were directly assayed onsite by gamma-ray spectrometry using the specially built and calibrated barrel counter. Thus, a total of 231 oil samples were gamma counted during this project. The results of the gamma analyses for the three samples (top, middle, and bottom) from each drum were averaged to represent the average drum concentration of the gamma-emitters. Cobalt-60 and ^{137}Cs were the major gamma-emitting radionuclides present. The distribution of the average drum gamma activity concentrations for all plants is shown in Figure 5. The statistics describing this distribution are as follows:

Arithmetic average	3.37E-4
Geometric mean	1.02E-5
Median	6.07E-6
Geometric standard deviation	17.6
Minimum	2.78E-8
Maximum	4.02E-3

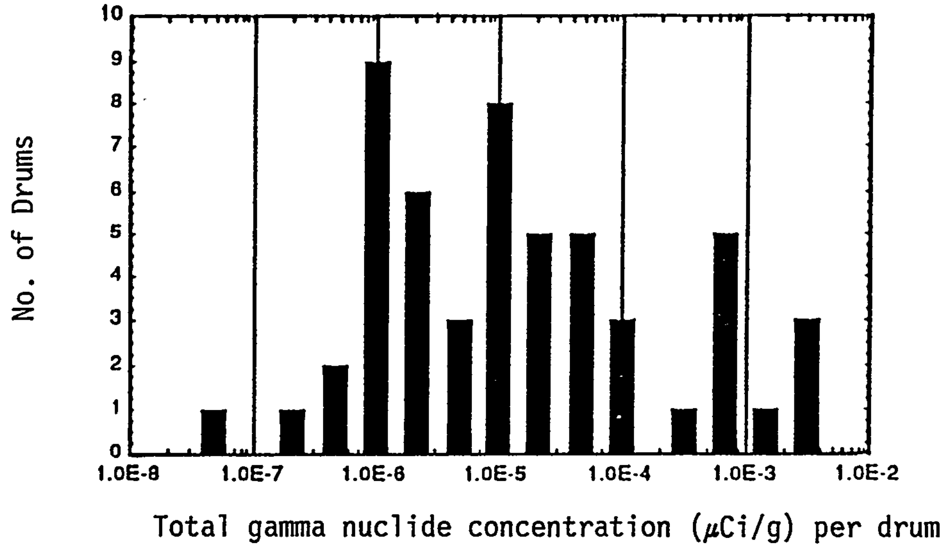

Figure 5. Distribution of Total Gamma-Emitting Radionuclide Concentrations in Oil Drums

To evaluate the radionuclide concentration variability within a drum of oil, the concentrations in the middle and bottom samples were divided by the concentration measured in the top sample. The majority of the drums indicated a moderate variability between the samples. This was particularly true for the ratio of middle-to-top samples. This distribution of the ratios of middle-to-top for all of the drums is shown in Figure 6. The average ratio for the middle-to-top samples was 1.4. The ratio of the bottom samples to the top showed a large variability for several of the drums. This distribution of the ratios of the bottom-to-top activity concentrations is presented in Figure 7. The average ratio for the bottom-to-top sample was 32.4. The drums which exhibited the largest variability were drums which contained a relatively small layer of water and sludge on the bottom of the drum. Because the layer of water or sludge was generally small, the use of the high activity concentration from the bottom sample as representative of one third of the drum volume would most likely conservatively overestimate the average radionuclide concentration in the drum.

Typical vertical distributions of the ^{60}Co and ^{137}Cs activity in four 208-liter drums of oil from PWR Station L, determined by direct assays with the Battelle barrel counter, are shown in Figures 8 and 9. Drum #32 displayed only a minor increase in radionuclide concentrations at the bottom 5 cm of the drum, with the activity being homogeneously distributed throughout the rest of the drum. Drum 17 showed maximum ^{60}Co and ^{137}Cs activities between 10 to 40 cm from the bottom of the drum, decreasing by a factor of about 100 at the top of the drum. Drum 19 showed the highest ^{60}Co concentration at the bottom of the drum, but another peak in the ^{60}Co and ^{137}Cs activity at a height of 40 cm from the bottom. The activities then dropped about two orders of magnitude between a drum height of 40 cm to the top of the drum. Drum 14 showed a steady increase in activity of about two orders of magnitude between the top to the bottom of the drum. The radionuclide distributions in Drums 14, 17, and 19 were typical of the higher activity level drums, and the distribution in Drum 32 was typical of the lower activity drums. They all, however, illustrate the non-homogeneous distribution of radioactive material in drums of contaminated oil and the problems of obtaining representative samples for quantifying the curie contents of the entire drum.

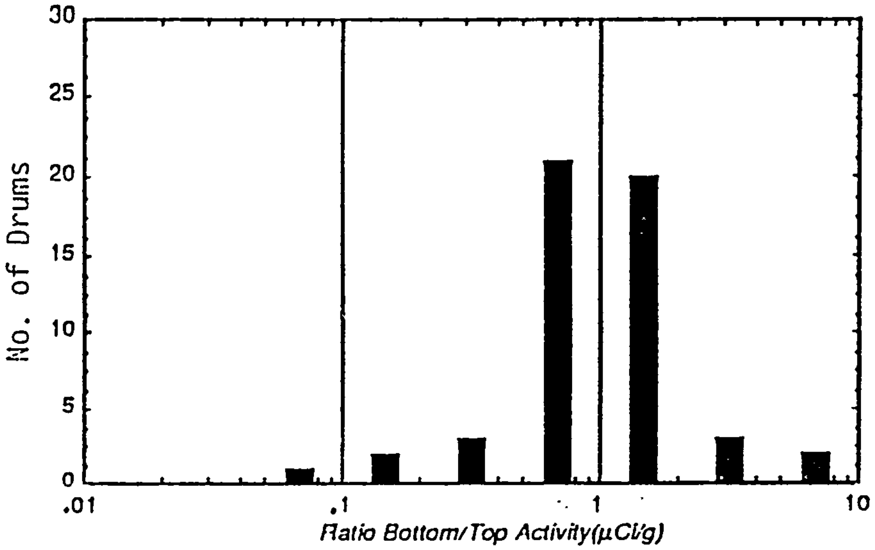

Figure 6 Ratio of Total Gamma Activity in Middle Oil Sample to Top Oil Sample from Each Drum (All Plants)

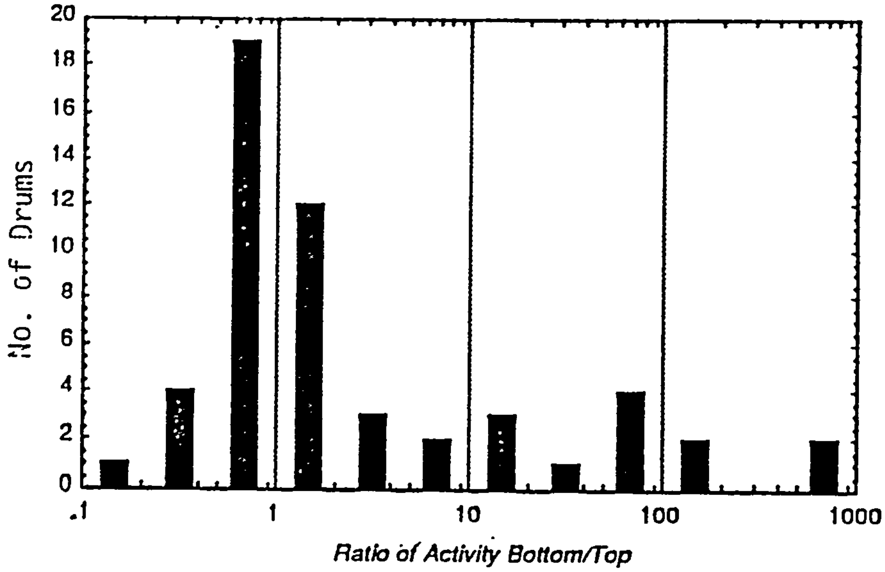

Figure 7 Ratio of Total Gamma Activity in Bottom Oil Sample to Top Oil Sample from Each Drum (All Plants)

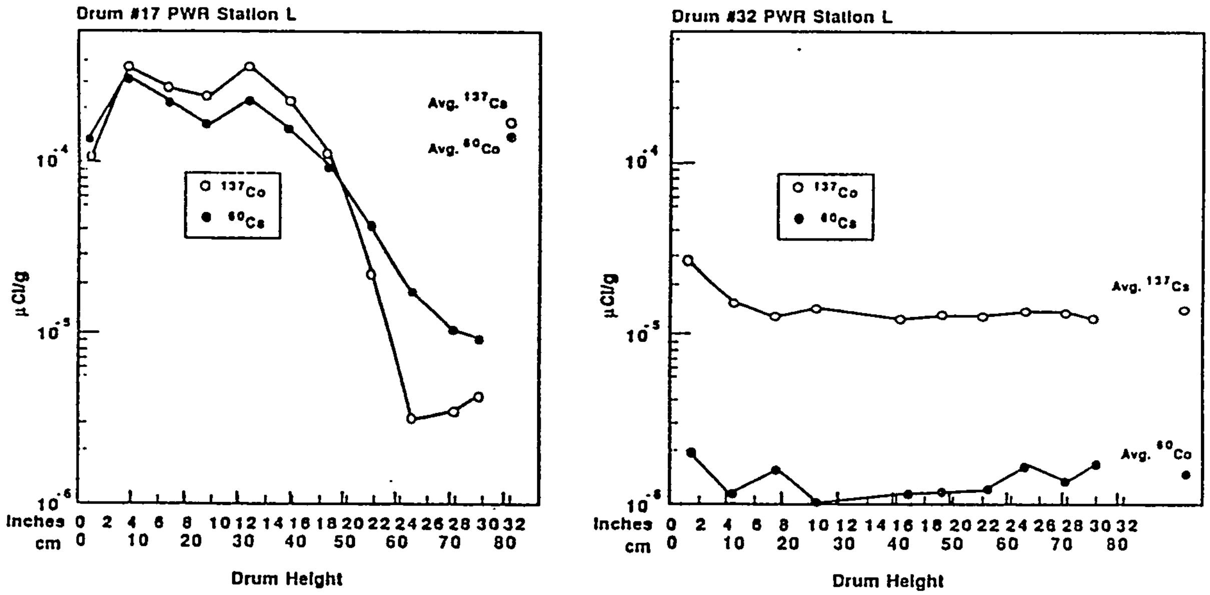

Figure 8 Vertical Distributions of ^{60}Co and ^{137}Cs in 208-Liter Drums of Oil by Direct Assay. Drums #32 and #17, PWR Station L

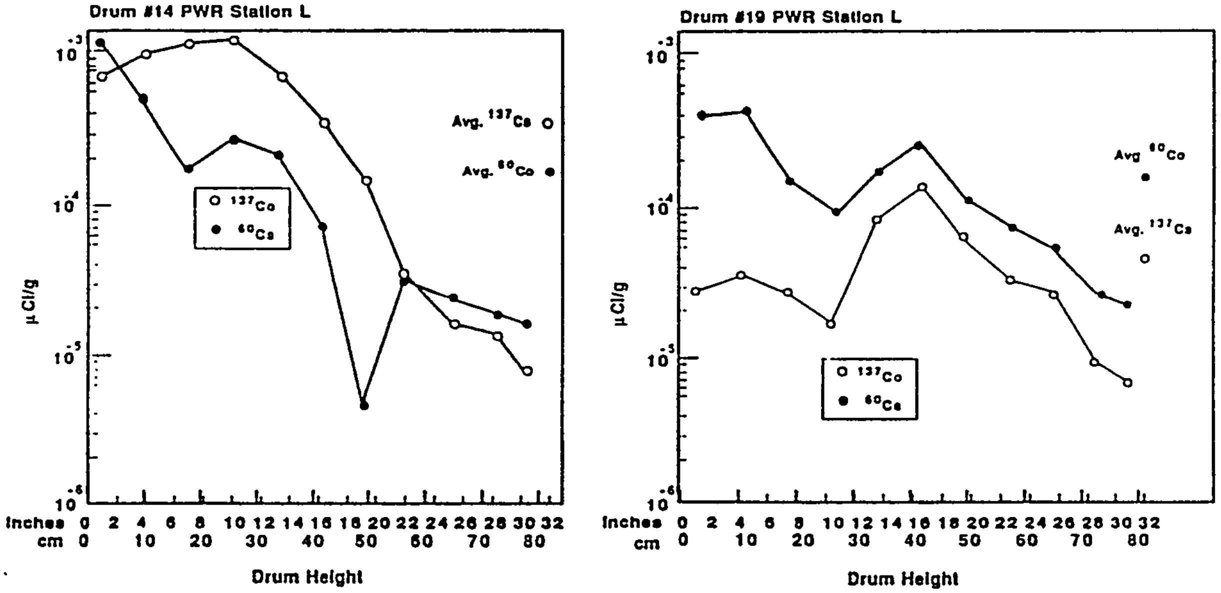

Figure 9 Vertical Distributions of ^{60}Co and ^{137}Cs in 208-Liter Drums #14 and #19, PWR Station L

To determine the reasonableness of assigning an average of the top, middle, and bottom samples as the average activity concentration of the total drum, ten drums of oil from two plants were subjected to direct gamma assay measurements using the Battelle barrel counter. In this device, the drums were scanned from top to bottom with a high-purity germanium detector as the drum rotated. The barrel counter integrated the counts from the scan to determine an average concentration in the drum. Due to the nature of the direct assay, the results should be highly representative of the true average concentration in the drum. Table 6 shows the result of the direct assay measurements, the grab sample results, and the comparison of the two average concentrations.

Table 6

Comparison of the Total Gamma Activity in Oil Drums by Grab Sampling Versus Direct Assay

Plant	Drum No.	Concentration, μCi/g Grab Sampling	Concentration, μCi/g Direct Assay	Grab/Direct
L	10	1.1E-6	6.0E-7	+ 1.8
L	15	1.9E-6	2.8E-7	+ 6.8
L	29	3.5E-6	4.7E-7	+ 7.4
L	30	6.3E-6	1.7E-5	- 2.7
L	31	9.6E-6	1.6E-6	+ 6.0
L	32	5.1E-5	2.0E-5	+ 2.6
B	203	5.7E-7	4.2E-6	- 7.4
B	235	4.0E-5	7.3E-5	- 1.8
B	236	5.4E-6	1.3E-5	- 2.4
B	237	5.0E-6	7.4E-5	-15.
Average		1.24E-5	2.04E-5	- 1.6

These results show reasonable agreement (within a factor of 1.6 to 2.7) between the two measurement methods for 6 of the 11 drums. They provide an indication that an average grab sampling of the top, middle and bottom of a drum of oil will usually provide a reasonable representation of the average activity concentration of the total drum. However, sampling errors of up to a factor of 6 to 15 are still evident, even after compositing the top, middle and bottom samples. Nevertheless, this sampling method is much better than taking a single grab sample, and should be acceptable for characterizing the radioactive material content of BRC spent oil. Perhaps a better sampling method would be to vigorously stir the oil in the drum before grab sampling, but this technique would require evaluation.

3.3 Secondary-Side Ion Exchange Resin

A total of 63 samples of secondary-side powdered ion exchange resins were collected from five PWR plants. Only PWR stations generate secondary side ion exchange resin wastes. The samples were analyzed at Battelle, Pacific Northwest Laboratories by gamma spectroscopy for the gamma nuclides, and radiochemistry measurements of the non-gamma emitting nuclides were performed. In addition, the Battelle barrel counter was taken to two of the plants and direct assays were performed onsite on a number of 208-liter drums of resin.

Generally, the resins were collected from the top of the drums of resin. It was assumed that the resins were reasonably mixed in the transfer and packaging steps. However, to assess the representativeness of the grab samples collected from drums of ion exchange resins, 13 out of 22 drums from a single plant were counted with the Battelle barrel counter. Table 7 shows the comparison of the gamma activity concentration measurements by grab sample and by direct assay.

The results of the comparison indicate that the grab sample measurements generally compare favorably with the direct assay results. For the powdered resins analyzed in this study, grab sampling provides a reasonable method for obtaining representative resin samples for radionuclide analyses if the resins are well mixed prior to drumming and do not fractionate while settling in the drums. The sampling problems for bead resins used in primary coolant and liquid radwaste cleanup may be more difficult than for powdered secondary coolant cleanup resins.

Table 7

Comparison of Grab Sample and Direct
Assay Measurements of Ion Exchange Resins

	Total Activity Concentration, µCi/g		Ratio
Drum No.	Grab Sampling	Direct Assay	Grab/Direct
R-58	5.2E.6	9.2E-6	-1.8
R-59	3.6E-5	1.1E-5	+3.3
R-60	1.9E-5	5.1E-6	+3.7
R-61	2.1E-6	1.5E-E	-7.1
R-62	4.5E-6	7.6E-6	-1.7
R-63	4.9E-6	8.5E-6	-1.7
R-64	4.6E-6	7.6E-6	-1.7
R-65	8.1E-7	7.2E-6	-8.9
R-66	1.4E-6	5.1E-6	-3.6
R-67	1.5E-6	3.9E-6	-2.6
R-68	2.4E-5	1.7E-6	+14.1
R-69	6.8E-7	3.6E-6	-5.3
R-70	2.8E-5	8.2E-6	+3.4
Average	1.02E-5	7.76E-6	+1.3

4. CONCLUSIONS

This study has highlighted some of the difficulties of conducting representative sampling of low-level waste streams (DAW, oil, and resin) for radionuclide analyses. These difficulties can be greatly minimized by applying the sampling and analyses techniques described in this paper, particularly for DAW and oil. The extreme variability in radionuclide concentrations and composition, and the patchiness of surface contamination associated with DAW can be effectively managed by utilizing bulk direct gamma spectrometric assays coupled with representative sampling which assures that the subsample has the same relative radionuclide composition of ^{60}Co and ^{137}Cs as the bulk material. The direct bulk assays of large quantities of DAW (e.g., 208-liter drums) average out the piece-by-piece variability of the radionuclide contamination, and by scaling-up the ^{60}Co and ^{137}Cs contents of the subsample to match the drum contents, a representative determination of the radiochemically measured nuclides on a bulk basis can be accurately made. The practice of sampling drums of contamination oil from the top, middle, and bottom of the drum to provide a composite sample has greatly improved the representativeness of radionuclide determinations of spent oil. Although the vertical distribution of ^{60}Co and ^{137}Cs in some oil drums varies by several orders of magnitude from top to bottom of the drums, the grab sampling and compositing of the top, middle, and bottom sections of the drum results in a composite sample having a radionuclide activity which is usually within a factor of 2 to 3 of the true total activity within the drum.

Grab sampling of thoroughly pre-mixed drums of powdered, secondary-side ion exchange cleanup resins was shown to provide reasonably representative samples for radionuclide analyses. However, obtaining representative samples of bead resins used for cleanup of the primary coolant and liquid radwaste streams may be much more difficult.

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MEASUREMENT METHODS FOR LOW-LEVEL ^{129}I DETERMINATIONS

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Abstract

The best methods for concentration measurements of low levels of ^{129}I and other very long-lived radionuclides present in nuclear wastes are based on techniques which do not require the measurement of radiation from the radionuclide. Radiochemical ^{129}I analyses based on chemical separations and counting require high radionuclide purity, have limited capability for checking the radionuclide purity, and have low sensitivity as a result of low ^{129}I specific activity. Other more selective and sensitive measurement methods developed and applied to ^{129}I analyses are neutron activation analysis (NAA), thermal emission negative ion mass spectrometry (TEMS) and accelerator mass spectrometry (AMS). These methods are at least a factor of 1,000,000 more sensitive than beta, x-ray, or gamma-ray counting methods. They are also very specific. All the methods require iodine separation from the sample prior to measurement but the more sensitive methods can use smaller sample sizes. A chemical separation method based on sample combustion, iodine trapping, and iodine purification is described. Iodine separations have been performed on a variety of solid, liquid, and off-gas waste samples. The measurement methods for the separated iodine are compared for application to low-level waste analyses. The NAA, TEMS, and AMS techniques have similar ^{129}I detection limits. Measurements by more than one method can be used to enhance quality assurance. The mass measuring instruments are also usable for ^{14}C and ^{99}Tc determinations on waste samples.

1. INTRODUCTION

The disposal of ^{129}I and other very long-lived radionuclides present in nuclear industry wastes requires concentration measurements at very low levels in a variety of samples. The measurements are required in order to determine the sources of ^{129}I and to estimate its environmental fate over millions of years. Laboratory studies of leaching rates also require sensitive measurements since low rates are desired and the experiment periods are short relative to the ^{129}I half-life of 16,000,000 years.

There are both natural and anthropogenic sources of ^{129}I. The natural sources result from cosmic ray reactions and natural fission.(1) The man-made sources result primarily from nuclear industry operations and nuclear explosions. Nuclear reactors produce fission product ^{129}I. Following its production a number of pathways can lead to the release or containment of the ^{129}I. A small fraction of the ^{129}I is distributed in the various reactor operation wastes. Some losses of ^{129}I have occurred as a consequence of reactor accidents. The major fraction of the ^{129}I remains in the irradiated fuel. Some ^{129}I is lost from the fuel during irradiated fuel storage. Reprocessing of irradiated fuel distributes the ^{129}I into the various separations plant gaseous, liquid and solid waste and effluent streams. Waste management activities can further distribute ^{129}I into different waste forms. Radioisotope production and usage also generates wastes and losses of ^{129}I. The volatility, solubility and chemistry of iodine results in partition of ^{129}I into many waste streams.

Global models have been developed for the natural iodine and ^{129}I cycle in nature.(1) (2) (3) Figure 1 shows the entry points where anthropogenic ^{129}I enters the iodine cycle. Nuclear explosions and the nuclear industry releases to the atmosphere have resulted in local, regional and global ^{129}I distribution.(4) Liquid wastes have discharged ^{129}I to the ground water, surface waters and oceans. Since iodine is very soluble, it migrates along water pathways. Burial of solid wastes can also result in ^{129}I releases to the environment. Once released to the environment ^{129}I accumulates on the surface or migrates with water and air flows. The dilution with natural iodine greatly reduces the specific activity of iodine as it enters and migrates in the iodine cycle. While this reduces the dose and risk from ^{129}I, it complicates the analytical radiochemistry for ^{129}I measurements of environmental samples.

Advances in analytical techniques for long-lived radionuclides have provided methods for measurement of ^{129}I concentrations and the $^{129}I/^{127}I$ isotopic ratio in a variety of sample types from nuclear industry process and waste streams to old iodine from deep water and mineral sources. This paper reviews the techniques available for measurements of ^{129}I in low-level waste and its migration from waste disposal sites.

2. SAMPLE COLLECTION

Figure 2 shows the decay scheme and gamma plus x-ray spectrum for ^{129}I. The low specific activity and low energies associated with ^{129}I radioactive decay and the presence of other radioactive nuclides have limited the application of direct in-line or in-plant measurements of ^{129}I to a few selected cases such as reprocessing plant stack gas monitors. Most ^{129}I measurements on low-level waste require laboratory analyses of representative samples. Samples which contain 10^8 to 10^9 atoms of ^{129}I (about 10^{-5} pCi) are adequate for the more sensitive measurement procedures.

Sampling of low-level waste can present special problems especially if an analysis is desired on heterogeneous materials, or if iodine must be collected from large volumes of aqueous or gaseous streams. Solid waste samples are often mixtures of materials which require very large samples or a large number of samples if representative results are to be obtained. Non-destructive radiation measurements of fission products can aid in sample selection and sub-sampling. Iodine volatility and mobility can result in rather selective iodine migration and thus laboratory verification of any assumed ^{129}I to other fission product correlations is essential. Most laboratory procedures can accommodate several hundred grams of sample material per analysis. Larger amounts require special apparatus and more labor.

Iodine samples can be collected on activated charcoal from large air and some other gas streams.(5) Activated charcoal should be selected which is free of KI or other iodine-containing additives frequently used for iodine containment by the nuclear industry. Unexposed charcoal should also be provided to the laboratory for blank ^{127}I and ^{129}I measurements.

Anion or mixed bed ion-exchange resins can be used to concentrate anionic iodine samples from large water and other dilute aqueous sources.(6) Many liters of water have been sampled by this technique to provide measurable ^{129}I. Several ion-exchange beds in series can be used to check for break-through.

3. ANALYTICAL RADIOCHEMISTRY

Measurement methods for ^{129}I usually require the separation of iodine from the sample matrix. This removes radioactive and/or chemical interferences in the measurement and reduces the sample to a volume and form compatible with the iodine isotopic analyses methods. A procedure which provides the required iodine separation and has been used with a large variety of process, waste and environmental samples is based on combustion of the sample or sample aliquot in oxygen and trapping of the iodine in the off-gas.(7) This iodine separation procedure is outlined in Figure 3. The sample is first spiked with a known amount of ^{125}I prior to any separations. The spike provides a means for determination of the chemical yield of the procedure and for isotopic dilution analysis for the other iodine isotopes present in the sample. Large liquid samples are then concentrated by anion exchange. The anion exchange resin containing the separated iodine is then processed the same as solid samples. Small liquid samples and solid samples are directly processed through the drying and combustion procedure. The iodine in the combustion off-gas is trapped on a small charcoal absorber. Heat and nitrogen flow are then used to process the iodine through the remainder of the combustion and iodine isolation procedure. The hydrated manganese dioxide provides a preliminary separation of iodine and bromine. The separated iodine is collected in a small volume (about 100 microliters) of dilute ammonia solution. The iodine solution is then prepared for isotopic analysis or further purified if required by a micro-extraction procedure.

The iodine separated from samples which contain several picocuries (about 10^{14} atoms) or more ^{129}I can be counted by low-level gamma spectrometry for ^{125}I and ^{129}I. Maximum counting sensitivity and selectivity are obtained with a well-type, high-resolution Ge detector in a low-background anticoincidence shield.(8) It is necessary that the ^{125}I spike activity and any other radioactivity be sufficiently low so as not to interfere with the ^{129}I 39.6 keV gamma peak. X-rays from the decay of ^{137}Cs and ^{125}Sb daughters can interfere with ^{129}I measurements. Standard ^{125}I, ^{129}I and ^{131}I solutions are available from the National Institute of Standards and Technology (NIST) for detector calibrations.

Low-level beta counting can also be used to measure a few picocuries or more of ^{129}I. No radioactive spike can be used to measure the radiochemical separation yield when beta counting measurements are used for ^{129}I analyses. There is also no way to check the radionuclide purity of the measured activity when beta counting. Thus beta counting methods can be used to set upper limits to the ^{129}I activity levels but may also overestimate the activity level if other radionuclides are present.

Most low-level ^{129}I analyses are currently being made by neutron activation analysis (NAA), thermal emission mass spectrometry (TEMS), or accelerator mass spectrometry (AMS).(7) (9) (10) These methods all have similar detection limits of about 10^7 atoms (10^{-6} pCi). The selection of measurement method depends on the facilities and equipment available to the laboratory and the $^{129}I/^{127}I$ ratio expected. Samples are sealed in quartz or other suitable containers for NAA. They are then irradiated with neutrons in an irradiation facility at a nuclear reactor. Following the reactor irradiation the samples are radiochemically processed to separate the iodine from other radioactivities produced during the irradiation. The major nuclear reactions of interest for activation analysis are shown on Figure 4 together with the ^{130}I decay scheme. The ^{130}I product of ^{129}I activation can be counted at very low levels since multiple gamma-rays are associated with its decay scheme. Several beta-gated multiple gamma coincidence systems have been developed for ^{130}I counting.(11) The ^{126}I or ^{128}I and ^{125}I activity levels are also determined. A comparator standard made from NIST standard reference material ^{129}I is irradiated with the samples and used to determine the ^{129}I concentration and iodine isotopic ratios by comparison of the sample and standard count rates. The ^{125}I count rate is used to correct for radiochemical yield.

Mass spectrometric iodine isotopic analysis requires a negative ion, thermal emission mass spectrometer. Figure 5 is a diagram of the PNL iodine mass spectrometer. The mass spectrometer uses a rhenium triple filament for negative thermal ionization. The center filament is coated with lanthanum hexaboride. The separated iodine as I^- from the sample is mounted and dried together with Ag+ on the two side filaments. Mass spectrometric $^{125}I/^{129}I$, $^{129}I/^{127}I$ and $^{125}I/^{127}I$ ratios are then determined. Isotopic dilution analysis calculations are used to estimate the ^{129}I and ^{127}I sample concentrations from the known ^{125}I spike activity. The mass spectrometric ratio measurements are absolute and require no calibration. The initial ^{125}I spike level is determined by a sum-coincidence method.(12) Both the ^{125}I and ^{129}I estimates are also periodically checked against the NIST standards. Thermal emission mass spectrometry has also been applied to ^{99}Tc analyses.(13)

Samples of iodine for AMS analysis are also mounted as AgI. Several milligrams are required so dilution with natural ^{127}I is sometimes used. Figure 6 is a diagram of the LLNL accelerator mass spectrometer.(14) Accelerator mass spectrometers have very low backgrounds and almost no interference problems making them ideal for very large isotopic abundance ratio measurements.(10) AMS is the only method suitable for $^{129}I/^{127}I$ analyses of natural ^{129}I and other samples greatly diluted with natural ^{127}I.(1) AMS is being used routinely for ^{14}C analyses; other long-lived isotopic measurements such as ^{129}I are performed periodically at several AMS laboratories.(15)

Another measurement method for ^{129}I under development uses the inductively coupled plasma mass spectrometer (ICPMS). Since ICP mass spectrometers are more widely available, the method would be easier for some laboratories to apply to iodine isotopic analysis if sufficient ^{129}I is available in the sample (about 0.01 pCi). ICPMS may be applicable to ^{99}Tc analysis. Atomic absorption spectrometry has also been used for technetium determinations.(16)

4. DISCUSSION

The selection of methods for ^{129}I analyses depends on the expected ^{129}I concentration, the $^{129}I/^{127}I$ ratio and the equipment and facilities available to the laboratory. Iodine separations are needed with most all methods. One exception is water which has been analyzed by mixing with ^{125}I spike solution and mounting on the TEMS filament without any chemical processing. Since considerable labor is required to obtain a reliable iodine separation from most waste samples, measurement by one of the methods which confirms the identity of ^{129}I is desired. Thus beta counting is not recommended.

Table 1 compares the detection limits and applicable natural iodine range for the various methods. If possible, method and sample size should be selected which provides at least a factor of ten above the detection limit. When a few pCi or more ^{129}I are available in the sample, gamma spectrometry can be used to estimate the ^{129}I level following an iodine separation from other activities. The effects of self-absorption on the weak ^{129}I gamma-ray must be considered in the sample counting and detector calibration.

The more sensitive and selective ^{129}I measurement methods are preferred when available. The NAA method has the largest range for both ^{129}I and ^{127}I and requires the least iteration when the magnitude of the ^{129}I level is unknown. The TEMS method requires that the $^{125}I/^{129}I$ be within measurable limits and that the sample size selected contains a few micrograms or less ^{127}I. This may require reruns or respiking if the initial estimates are spurious by several orders of magnitude. When assured quality is needed at levels near the detection limit both NAA and TEMS can be used on portions of the iodine separated from the sample. The potential interferences are different for the two methods and provide good confirmation for each other.(7)

Since there is limited AMS ^{129}I measurement capability, the method is normally used for samples with very small $^{129}I/^{127}I$ ratios. The method is not required for most waste samples, but has advantages for disposal site pre-use surveys and associated geochemical research.

Some ^{129}I PNL analysis results for typical sample types are summarized in Table 2. The ^{129}I concentration and $^{129}I/^{127}I$ atom ratio ranges illustrate the magnitude of values to be expected. The number of power reactor wastes analyzed to-date is small and the ranges may be larger than indicated. The data shows that ^{129}I counting methods do not have the sensitivity required for many low-level waste analyses if actual values rather than upper limits are needed. The more sensitive methods also provide iodine isotopic ratio values which are significant in any risk evaluation.

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TABLE 1. COMPARISON OF ^{129}I MEASUREMENT METHODS

Method	Detection Limit Atoms	Detection Limit pCi	Detection Limit $^{129}I/^{127}I$ Atoms	Range ^{127}I	Comments
Counting	2×10^{13}	0.5		<mg	Gamma spectrometry
ICPMS	3×10^{11}	0.01	$\geq 1 \times 10^{-6}$		Under development
NAA	1×10^{7}	4×10^{-7}	$\geq 1 \times 10^{-10}$	<10 g	Large application range
TEMS	1×10^{7}	4×10^{-7}	$\geq 1 \times 10^{-8}$	<ug	More precise
AMS	2×10^{6}	8×10^{-8}	$\sim 1 \times 10^{-13}$	>1-10 mg	Natural samples

TABLE 2. RANGES OF ^{129}I CONCENTRATIONS AND $^{129}I/^{127}I$ ATOM RATIOS FOR TYPICAL ANALYSES TO-DATE

Description	^{129}I Concentration Ranges		$^{129}I/^{127}I$ Atom Ratio Ranges
Hanford Region Air	1×10^{6} - 5×10^{10} atoms/SCM	3×10^{-8} - 2×10^{-3} pCi/SCM	1×10^{-7} - 1×10^{-2}
Columbia River	4×10^{7} - 2×10^{10} atoms/l	1×10^{-6} - 7×10^{-4} pCi/l	2×10^{-9} - 4×10^{-6}
Ground Water	7×10^{6} - 1×10^{17} atoms/l	2×10^{-7} - 3×10^{3} pCi/l	1×10^{-9} - 1×10^{-1}
Power Reactors Soil	3×10^{7} - 8×10^{8} atoms/g	1×10^{-6} - 3×10^{-5} pCi/g	5×10^{-9} - 7×10^{-8}
Power Reactors LLW *	3×10^{7} - 3×10^{11} atoms/g	1×10^{-6} - 1×10^{-2} pCi/g	8×10^{-7} - 3×10^{-4}

* Low-level waste

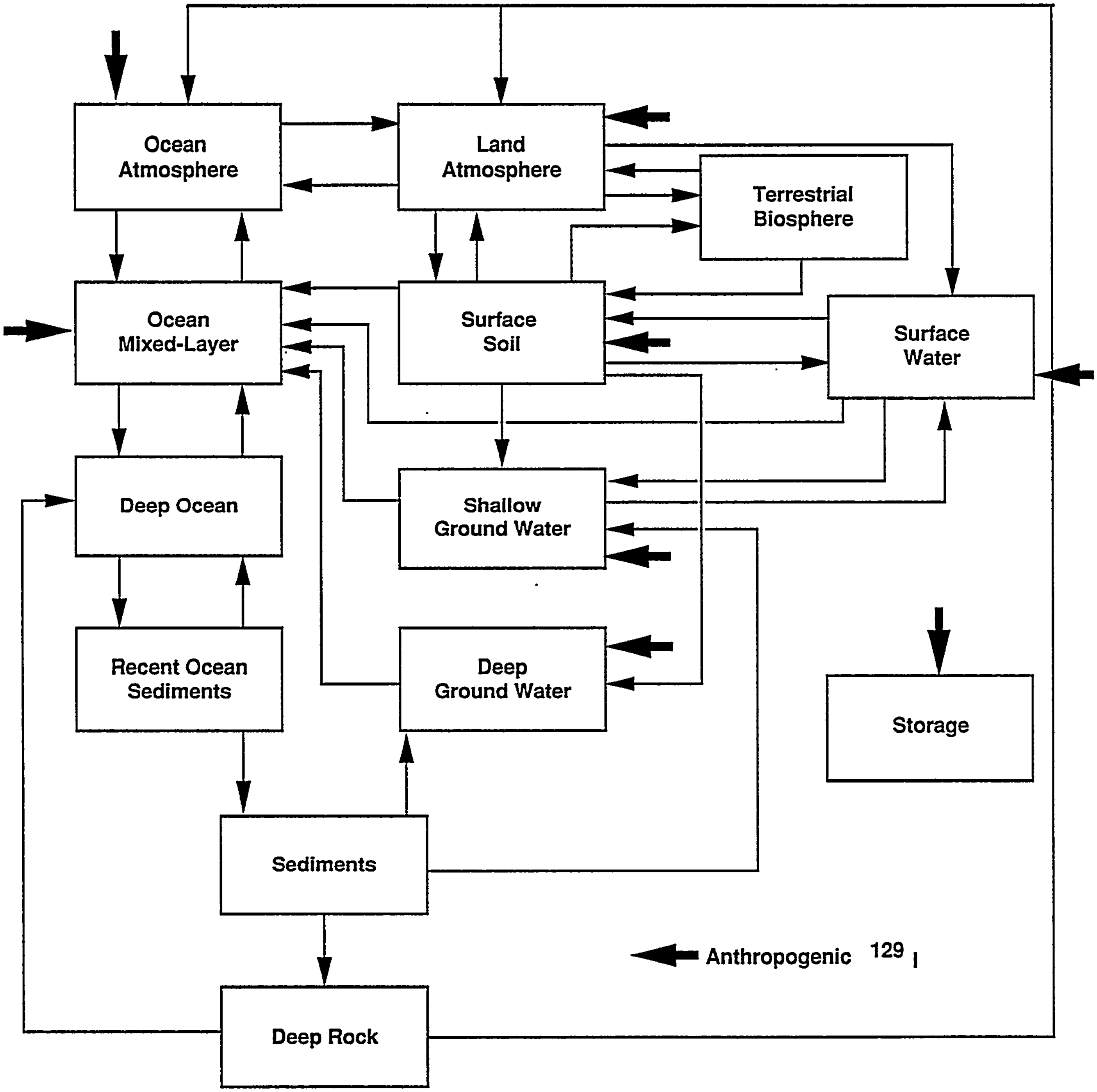
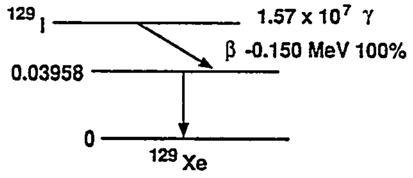


Figure 1. Global iodine model showing major points where anthropogenic ^{129}I enters the iodine cycle.



Radiation	Energy (MeV)	Intensity (%)	Relative Intensity to K_{α_1}	Conversion Coefficients
γ	0.03958 ± 0.0003	7.52		α_K 10.5 α_{LM} 1.8 α_T 12.3
x (K_{α_1})	0.02978	37.0	1	
x (K_{α_2})	0.029458	19.9	0.537	
x ($K_{\beta_1}^1$)	0.03360	10.8	0.292	
x ($K_{\beta_2}^1$)	0.03442	2.4	0.064	
β^-	0.150 ± 0.005			

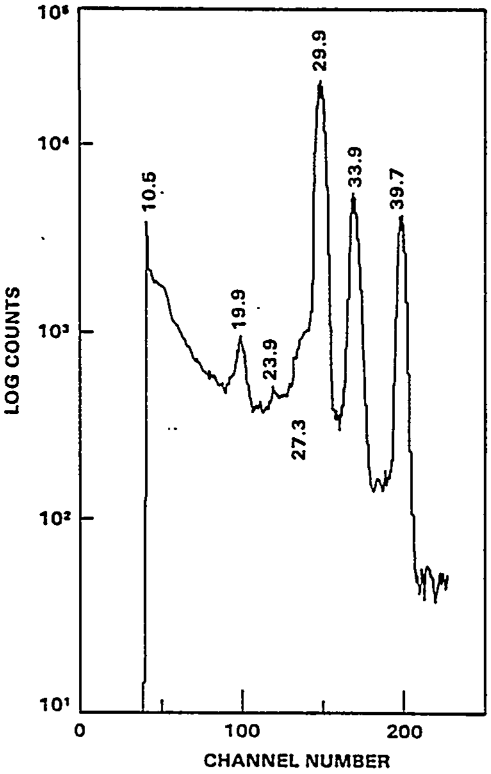


Figure 2. Decay information and spectrum for ^{129}I radioactive decay. The spectrum was taken in a well-type Ge detector (energies in keV).

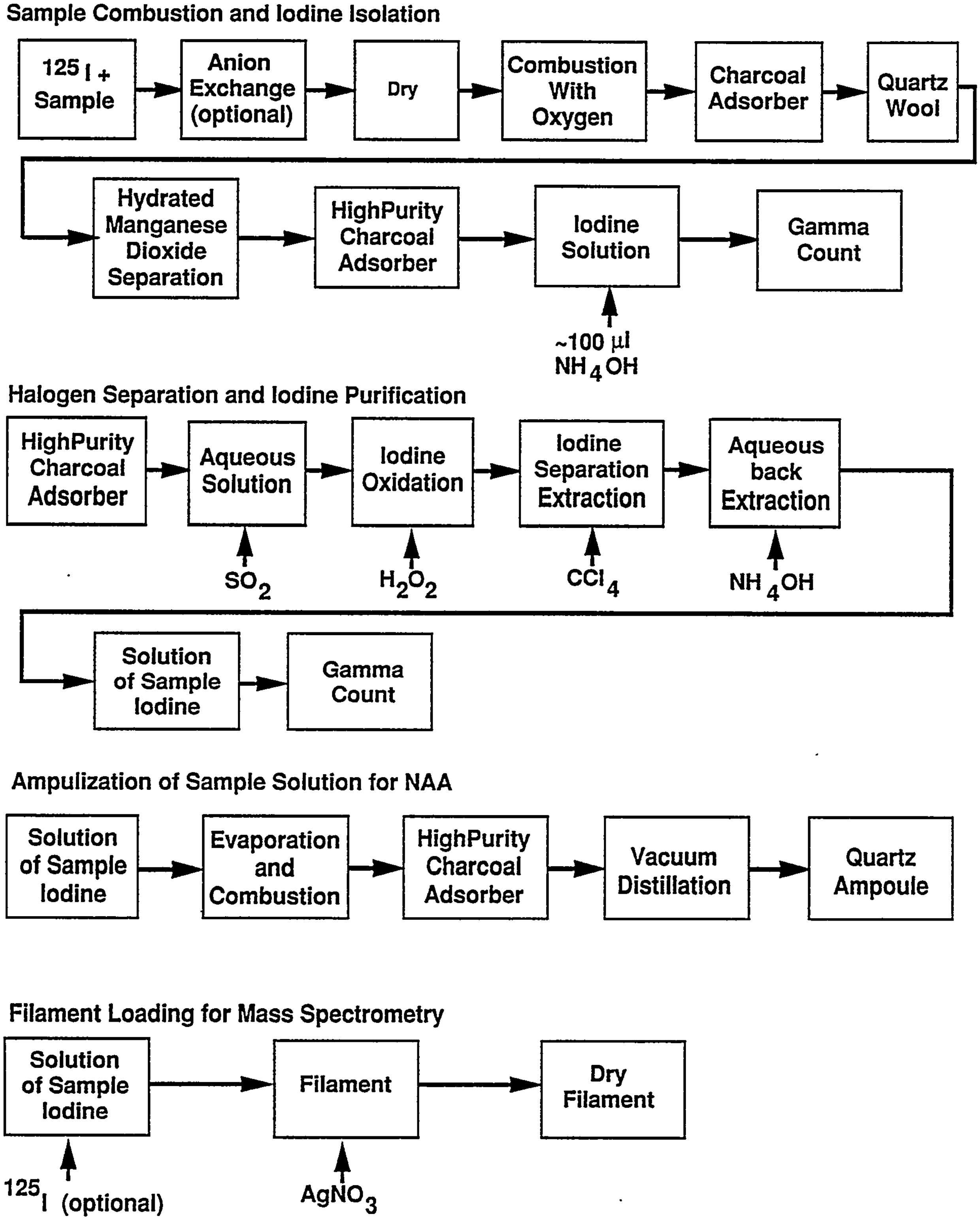


Figure 3. Radiochemical procedure for separation of iodine prior to isotopic analysis.

$$^{127}\mathrm{I}(n,\gamma)\,^{128}\mathrm{I} \xrightarrow[\text{25 MIN}]{\beta^{-},\gamma} {}^{128}\mathrm{Xe}$$

$$^{127}\mathrm{I}(n,2n)\,^{126}\mathrm{I} \xrightarrow[\text{13 Day}]{\beta^{-},\gamma} {}^{126}\mathrm{Xe}$$

$$^{129}\mathrm{I}(n,\gamma)\,^{130}\mathrm{I} \xrightarrow[\text{12.4 HR}]{\beta^{-},\gamma} {}^{130}\mathrm{Xe}$$

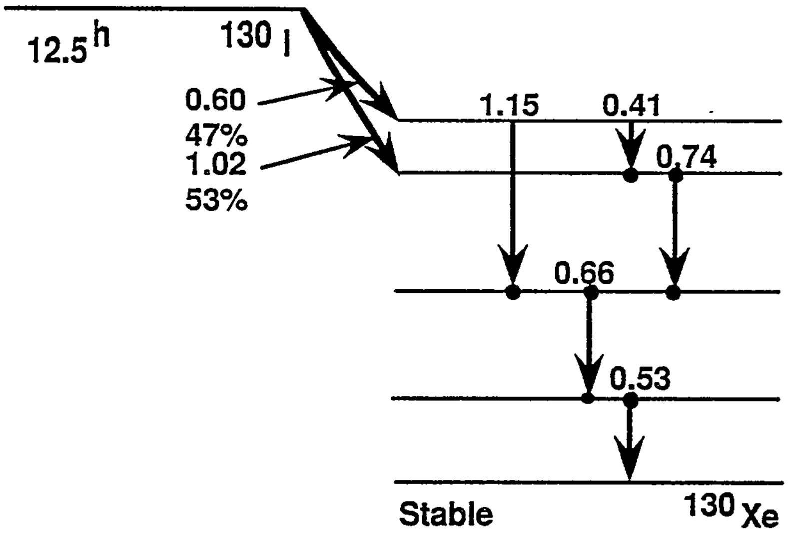


Figure 4. Major reactions for ^{129}I neutron activation analysis and ^{130}I decay scheme showing multiple gamma-ray transitions (energies in MeV).

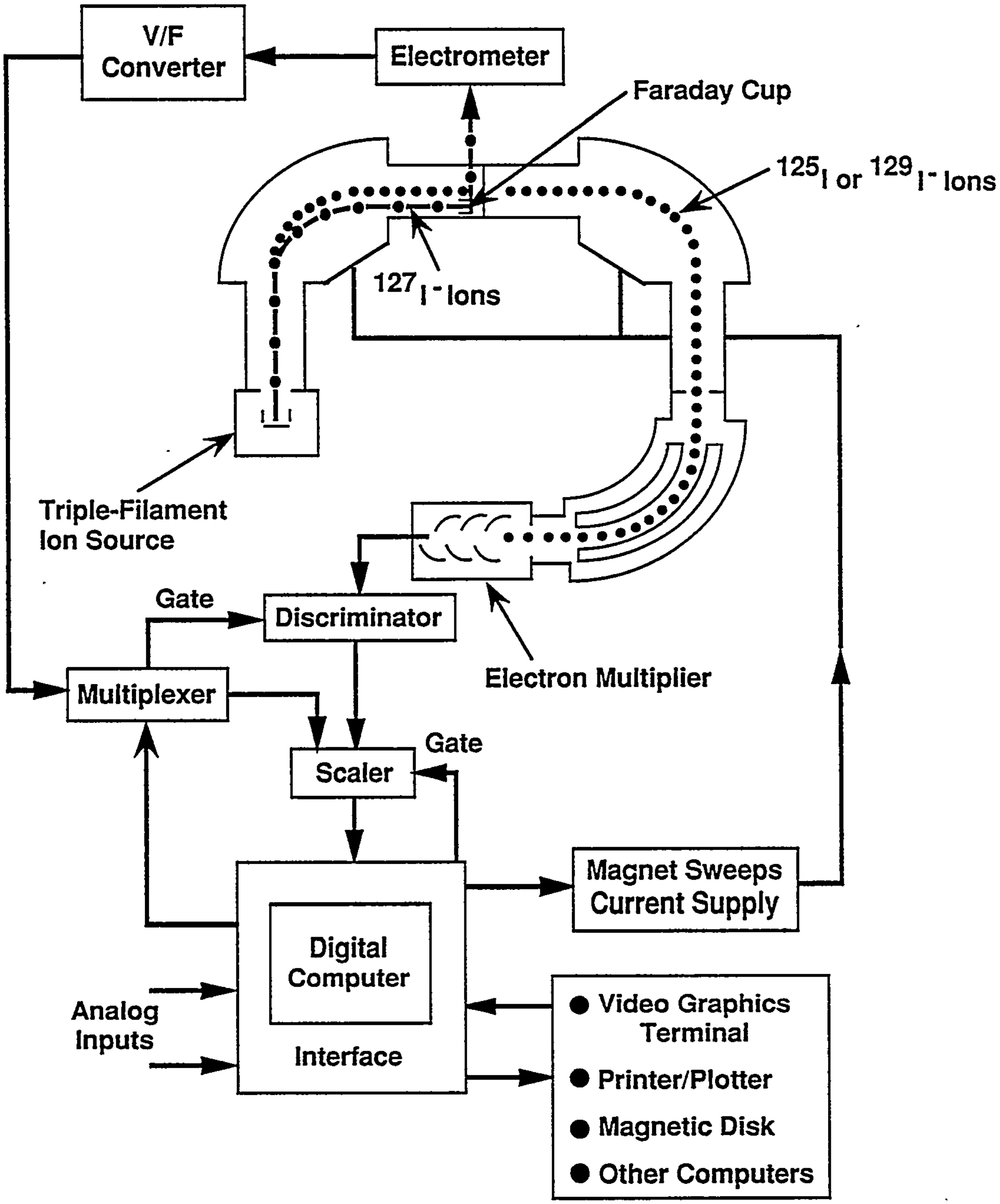


Figure 5. Diagram of negative ion, thermal emission mass spectrometer used for ^{129}I analysis.

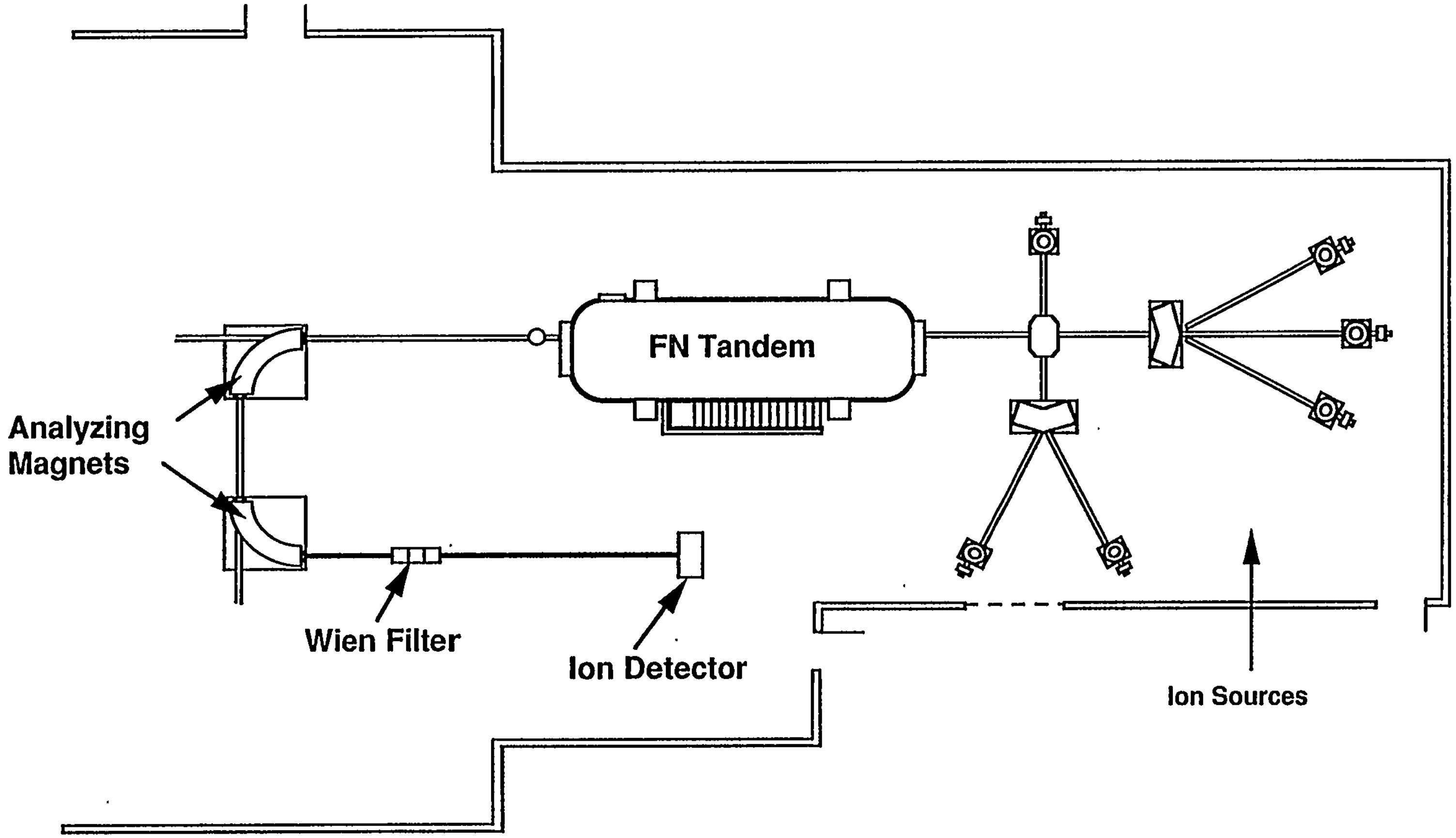


Figure 6. Diagram of an accelerator mass spectrometer (LLNL) for long-lived radionuclide analysis.

RELIABILITY OF CHEMICAL ANALYSES OF WATER SAMPLES

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ABSTRACT

Ground-water quality investigations require reliable chemical analyses of water samples. Unfortunately, laboratory analytical results are often unreliable. The Uranium Mill Tailings Remedial Action (UMTRA) Project's solution to this problem was to establish a two phase quality assurance program for the analysis of water samples. In the first phase, eight laboratories analyzed three solutions of known composition. The analytical accuracy of each laboratory was ranked and three laboratories were awarded contracts. The second phase consists of on-going monitoring of the reliability of the selected laboratories.

The following conclusions are based on two years experience with the UMTRA Project's Quality Assurance Program.

- The reliability of laboratory analyses should not be taken for granted.
- Analytical reliability may be independent of the prices charged by laboratories.
- Quality assurance programs benefit both the customer and the laboratory.

INTRODUCTION

The purpose of the Department of Energy's UMTRA Project is to reduce or eliminate the hazards posed by inactive uranium mill tailings. One hazard is the contamination of ground water by heavy metals, radionuclides, and reagents leached from the tailings.

Major Project objectives are to determine the extent of existing ground-water contamination, and to predict the effects of remedial actions on future ground-water quality. Meeting these objectives requires reliable chemical analyses of water samples. When the Project began, the reliability of laboratory analyses was taken for granted. Laboratories were awarded contracts on the basis of laboratory visits by Project quality assurance personnel. During these visits, the laboratory's internal quality control program and the qualifications of key laboratory personnel were checked. The contracted laboratories also participated in state or EPA sponsored water-quality performance evaluation programs. However, it soon became apparent that this was not sufficient. Laboratories often submitted sample analyses having cation-anion balances greater than 50 percent. When solutions of known composition were sent to the laboratories, the reported results were often wrong by a factor of more than ten.

These unreliable results caused the UMTRA Project to establish a two-phase quality assurance program for the analysis of water samples. At the same time, it was recognized that reliable analyses of improperly taken samples were also of little value. Therefore, a stringent set of protocols designed to assure proper sampling and field testing of water samples was implemented.

In the first phase of the program, eight laboratories participated in a pre-qualification. Each laboratory analyzed three solutions of known composition. The accuracy of each laboratory analyses was scored and three laboratories were selected to receive contracts.

The second phase consists of monitoring the reliability of analyses submitted by the selected laboratories. This phase will continue as long as the Project requires analyses of water samples.

PHASE ONE: PRE-QUALIFICATION

The purpose of the pre-qualification was to find at least three laboratories that could provide the Project with reliable analyses. This phase consisted of several steps.

First, initial accuracy criteria were established (Table I). These criteria were based on project requirements and what it was hoped most laboratories could achieve. The criteria were reviewed by personnel at the Pacific Northwest Laboratory, the Nuclear Regulatory Commission and Bendix Field Engineering Corporation. Some reviewers stated that the criteria should be species specific, although they could not specify which species should be subjected to more or less stringent criteria. Therefore, it was decided that if the criteria were to be revised, the revision would occur after evaluating the performance of laboratories participating in the pre-qualification.

In the second step, laboratories were invited to participate in the pre-qualification through an advertisement in the Commerce Business Daily. Thirteen laboratories chose to participate.

Thirteen sets of solutions of known composition were then prepared by Bendix. Each set consisted of three samples, each of which contained varying concentrations of all of the constituents listed in Table I. The sets sent to each laboratory were identical. Bendix provided the Project with the known concentrations of constituents in each solution as well as the uncertainties associated with the preparation of each solution. The known values and uncertainties were used to calculate an acceptable range for each constituent:

Acceptable range =

$$\frac{X(1-U)}{\frac{E+1}{100}} \text{ to } \frac{E+1}{100} X\ (1+U) \quad \text{(Eqn.1)}$$

where:

X = known concentration (mg/L).
U = uncertainty associated with preparation of known solution.
E = allowable error (from accuracy criteria, Table I).

Eight of the thirteen laboratories submitted analytical results. Their results were evaluated according to the initial accuracy criteria. This evaluation made it clear that some of the criteria were too stringent and needed to be revised. The revised criteria reflected the analytical abilities of the laboratories while preserving the accuracy required to meet Project objectives. The constituents were divided into three groups (Table I).

- Group 1 contains the toxic trace constituents that are commonly associated with uranium mill tailings. The criteria for Group 1 constituents were not revised.
- Group 2 contains most of the trace constituents not included in Group 1.
- Group 3 contains the major ions and the trace constituents that may control leachate chemistry.

The revised criteria were used to score the eight responding laboratories. When analytical results were not within the acceptable range, or results were not reported, an unacceptable result was recorded. The laboratories scored 77, 74, 72, 70, 69, 46, 31, and 16 percent acceptable results. A summary of the pre-qualification results is given in Table II.

Sixty seven percent of all analyses were within the acceptable range. Sixty percent of the reported values were higher than the known concentration. The laboratories performed best when analyzing for TDS, zinc, tin, and most radionuclides. More than 50 percent of analyses for most of the common ions and toxic metals were acceptable. Iron and aluminium were among the constituents for which the laboratories performed most poorly. Both of these metals exert a strong influence on leachate chemistry.

It should be noted that the pre-qualification analyses were probably more accurate than most analyses performed by the laboratories. This is because they knew they were being tested and the known solutions were made with very pure materials which minimized analytical interferences. The results of the pre-qualification clearly showed the need for independent checks of analytical reliability after laboratories were selected to receive contracts.

The five laboratories with the top scores were visited by Project personnel. After considering quality control procedures, equipment, space, and personnel qualifications, three laboratories were selected to receive contracts. Although the cost of analyses was not considered in the selection process, there were large differences among the three laboratories.

PHASE TWO: POST-LABORATORY SELECTION MONITORING

The purpose of this phase is to monitor the reliability of analyses reported by the three laboratories selected in the pre-qualification. The laboratories agreed to the following conditions.

- o Complete analytical results would be submitted to the Project within five weeks of receiving each sample set.
- o The acceptability of analytical results would be judged by the Project according to pre-established cation-anion balance and accuracy criteria. There would be no payment for unacceptable results.

Cation-anion balance criterion

The analysis of a sample is unacceptable if the absolute value of the cation-anion balance is greater than five percent. The cation-anion balance is calculated as follows.

$$\text{Balance} = \frac{\text{meq Cations} - \text{meq Anions}}{\text{meq Cations} + \text{meq Anions}} (100) \quad \text{(Eqn.2)}$$

The balance is calculated using every constituent which contributes more than 0.1 percent to the sample's total dissolved solids content. If redox sensitive constituents are used in the balance, the balance is calculated for both oxidizing and reducing conditions and the laboratory is given the benefit of the doubt. Alkalinity, a major contributor to the balance, is measured in the field by Project personnel. The alkalinity value is not given to the laboratory. The laboratory is required to re-analyze those samples which do not satisfy the balance criterion. The laboratory is not paid for analyzing these samples until re-analysis results in a balance of less than five percent.

Accuracy criteria

Each sample set is divided into lots consisting of no more than nine field samples and at least one solution of known composition (Figure 1). Known solutions are disguised as field samples. The value reported for a constituent in a known solution is compared to the acceptable range of values for that constituent. The acceptable range is calculated from equation 1. When the analysis of a constituent in a known solution does not fall within the acceptable range, the laboratory is required to re-analyze the entire lot for that constituent. The laboratory is not paid for that constituent until re-analysis produces acceptable results.

In addition to monitoring cation-anion balances and accuracy, analytical precision is monitored by including at least four replicates of a field sample in each sample set sent to the laboratory. The replicates are disguised as individual samples. The coefficient of variation is calculated for each constituent in the set of replicates and compared to the precision criteria shown in Table III. The precision criteria are based on the degree of accuracy required for each constituent. When replicate analyses exceed the coefficients of variation, the laboratory is notified. This information helps the laboratory identify and correct analytical problems. Payment is not withheld.

The evaluation of laboratory performance indicates that initial analytical results are often unreliable. Decisions based on these analyses could lead to costly mistakes. Re-analysis usually results in data that are significantly more reliable. Both the Project and the laboratories benefit from the monitoring program. The Project gets more reliable data, and the laboratories are able to improve the quality of their work. In general, the reliability of analyses has improved over time.

CONCLUSIONS

Based on the experience of the UMTRA Project, the following conclusions are made:

1. The reliability of laboratory analyses cannot be taken for granted. Reliability is not necessarily guaranteed by laboratory in-house quality control programs or by a laboratory's participation in State or EPA water-quality performance evaluation programs.

2. Quality assurance programs benefit both the client and the laboratory. The client gets more reliable results, and the laboratory is able to identify and correct analytical problems.

3. The reliability of analyses and the quality of service provided may be independent of the prices charged by a laboratory.

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TABLE I

ACCURACY CRITERIA

Group	Concentration of constituent in known concentration (mg/L)	Acceptable error, in percent
I*	<0.01	100
	>0.01, <0.1	50
	>0.1, <1.0	25
	>1.0	10
II	<0.01	200
	>0.01, <0.1	100
	>0.1, <1.0	50
	>1.0	20
III	<0.01	200
	>0.01, <0.1	100
	>0.1, <1.0	50
	>1.0	10

*The initial accuracy criteria for all constituents were identical to the Group I criteria

Group I:	Sb, As, Ba, Ca, Cr, Pb, Hg, Mo, Se, U, Pb-210, Po-210, Ra-226, Ra-228, Th-230.
Group II:	B, CN, H_2S, NH_4, NO_2, PO_4, Co, Cu, Ni, Ag, Sr, Sn, V, Zn, TOC.
Group III:	Cl, SO_4, NO_3, Na, K, Mg, Ca, F, Al, Fe, Mn, SiO_2, TDS.

TABLE II

SUMMARY OF PRE-QUALIFICATION RESULTS[1]

Analyte	Known concentration (mg/l)	Acceptable range (mg/l)	Range of reported values (mg/L)	Percent reported values acceptable
Ca	636. ± 1.1%	572 - 707	285 - 865	29
K	5.72 ± 1.1%	5.14 - 6.36	5.24 - 7.64	71
Mg	55.9 ± 1.1%	50.3 - 62.2	50.0 - 99.8	57
Na	33.0 ± 1.1%	29.7 - 36.7	24.2 - 41.4	71
Cl	206. ± 1.0%	185 - 229	200 - 245	86
F	0.987 ± 2.0%	0.645 - 1.51	0.80 - 1.57	86
SiO_2	6.85 ± 2.8%	6.05 - 7.75	2.16 - 7.0	43
SO_4	1520 ± 2.0%	1350 - 1710	1450 - 1740	86
Dissolved Solids	3200 ± 2.5%	2840 - 3610	2970 - 3600	100
Al	0.126 ± 1.2%	0.083 - 0.191	<0.05 - 3.75	0
Fe	0.126 ± 1.2%	0.083 - 0.191	0.149 - 0.42	43
Mn	0.126 ± 1.2%	0.083 - 0.191	0.025 - 0.16	86
Ag	0.076 ± 1.2%	0.050 - 0.115	0.015 - 0.12	57
As	0.088 ± 1.2%	0.058 - 0.134	0.039 - 0.106	83
Ba	0.114 ± 1.2%	0.09 - 0.144	<0.05 - 0.54	33
Cd	0.076 ± 1.2%	0.050 - 0.115	0.020 - 0.090	86
Cr	0.076 ± 1.2%	0.050 - 0.115	<0.05 - 0.27	71
Hg	0.076 ± 1.2%	0.050 - 0.115	0.026 - 0.074	75
Mo	0.033 ± 1.2%	0.022 - 0.050	0.011 - 0.14	43
Sb	0.01 ± 1.2%	0.007 - 0.015	0.009 - 0.032	83
Se	0.076 ± 1.2%	0.050 - 0.115	0.055 - 0.102	100
*Pb-210	4.8 ± 7.0%	2.23 - 10.3	1.9 - 7.2	75
*Po-210	17.1 ± 3.0%	8.22 - 35.2	1.1 - 25.0	88
*Ra-226	10.0 ± 1.4%	4.93 - 20.3	5.7 - 14.9	100
*Ra-228	14.8 ± 7.0%	6.88 - 31.7	5.86 - 86.2	62
*Th-230	13.5 ± 2.3%	6.59 - 27.6	8.0 - 20.0	100
U	0.076 ± 1.2%	0.050 - 0.115	0.007 - 0.49	75
Co	0.101 ± 1.2%	0.067 - 0.153	0.088 - 0.36	71
Cu	0.101 ± 1.2%	0.067 - 0.153	0.015 - 0.20	71
Ni	0.101 ± 1.2%	0.067 - 0.153	0.09 - 0.28	71
Sn	0.050 ± 1.2%	0.025 - 0.101	0.044 - 0.075	100
Sr	0.176 ± 2.9%	0.115 - 0.272	0.178 - 0.6	57
Zn	0.101 ± 1.2%	0.067 - 0.153	0.084 - 0.15	100

TABLE II (continued)

Analyte	Known concentration (mg/l)	Acceptable range (mg/l)	Range of reported values (mg/L)	Percent reported values acceptable
B	0.088 ± 1.2%	0.043 - 0.178	<0.01 - 4.0	50
S	22.9 ± 2.5%	17.9 - 29.3	1.1 - 45	57
ALK	16.1 ± 0.7%	14.5 - 17.8	14.3 - 21.6	43
CN	0.59 ± 4.2%	0.38 - 0.92	0.13 - 0.91	83
TOC	1.46 ± 1.0%	1.16 - 1.84	1.5 - 4.0	33

*units = pCi/L

(1) Each laboratory analyzed three solutions with total dissolved solid concentrations of mg/L, 3200 mg/L, and mg/L. This table sumarizes the results of the 3200 mg/L solution.

TABLE III

PRECISION CRITERIA

Acceptable percent error for constituent	Maximum coefficient of variation
200	1.38
100	0.84
50	0.45
20	0.18
10	0.09

TABLE IV

LABORATORY PERFORMANCE, POST-SELECTION MONITORING

ACCURACY CRITERIA			
Laboratory	A	B	C
Number of known constituents analyzed	354	1543	274
% acceptable analyses			
Initial analysis	83	82	68
1st re-analysis	90	96	80
2nd re-analysis	—	99.5	—

BALANCE CRITERION			
Number of samples analyzed	145	495	73
% Acceptable analyses			
Initial analysis	90	83	45
1st re-analysis	92	91	65
2nd re-anlysis	—	96	—

WASTE MANAGEMENT AND QUALITY ASSURANCE REASONABLE CO-EXISTENCE?

James F. Bresson
Dames & Moore

Implementing Chapter III, Low-Level Waste Management, of DOE Order 5820-2, "Radioactive Waste Management" has created a major change in the operating philosophy of DOE's prime contractors. So has the decision of May 1, 1987, when it was made clear that EPA has regulatory authority over DOE's mixed waste. Suddenly two additional items became clear. First, DOE and its contractors were going to learn more about composition of low-level and low-level mixed waste than ever before. Second, low-level waste management was about to become a more focused, formal program, complete with needs for: 1) waste form identification, 2) program documentation; and 3) assurance that DOE's waste does in fact comply with applicable requirements. The importance of the above items is clearly emphasized by the inclusion of Data Quality Objectives in the Waste Acceptance Criteria section of DOE 5820-2 Chapter III guidance called "Data Quality Objectives", (DQO).

Simply put, the purpose of the DQO is to identify the quality (and quantity) of information necessary to convince a regulator or decision maker that enough is known about DOE's low-level and low-level mixed waste to allow safe disposal. The main objectives of the DOE and EPA shallow land burial requirements are to: 1) generate, with documented evidence, waste forms which are chemically inert and immobile, such that the waste will not tend to move about in the disposal medium; 2) select a disposal medium which would not let the wastes move about anyway; and 3) build some barriers around the wastes as emplaced in burial grounds, to provide additional assurance that buried wastes will stay in place. Compliance with these requirements must be demonstrated by quality data which describes the entire series of compliance activities.

Can this task be accomplished? Can we ever generate enough meaningful data to satisfy our regulators? Our critics? Intervenors? How many tests and analyses are needed to provide reasonable assurance that buried wastes present acceptable risks? When does data stop being useful, and become data for data's sake? And can meaningful Quality Assurance be applied to waste activities?

Following are descriptions of early attempts to relate QA to waste activities.

It is somewhat unfortunate that the first attempts to apply QA to waste management activities occurred when the WIPP site selection process was nearly complete, so that suddenly, a reasonably good site characterization process was made to look bad. Records and data requirements were imposed at the end of the site selection process, and an NQA-1 formatted program was applied at the last minute to nearly completed work and data. Rule Number One of Quality Assurance was violated. Items important to quality must be identified <u>before</u> activities commence, not somewhere downstream in the process. To be effective, QA plans must provide early direction and guidance.

QA Rule Number Two was violated during WIPP design. In a never-ceasing effort to take and use existing programs, whether they fit or not, instead of creating programs which meet specific needs, DOE immediately adopted in toto, the existing QA program for siting, construction and operation of reactors and production facilities, 10 CFR 50, Appendix B. It was a poor fit. Aside from site investigation, (already discussed), there is no real similarity between WIPP and a reactor. Although the 18-20 NQA-1 elements are so broad that they can be applied in some way to nearly any activity, early application of NQA-1 requirements to WIPP design was a disaster. Lesson Two: Create QA programs which are directly applicable to the programs to which they will apply.

The first attempt to create a QA program specific to waste management activities was the WIPP waste certification program. Waste Acceptance Criteria (WAC) were adopted. The WAC were not perfect, but they were at least specific to TRU waste, the waste for WIPP. More importantly, a specific QA manual was written related to 10 CFR 50, Appendix B and NQA-1, containing 18 applicable elements, but with words and requirements applicable to TRU waste management. The WAC and the QA manual provided guidance to the TRU program. QA plans and certification plans were written by TRU waste generators, reviewed, and approved by the WIPP-WAC Certification Committee. The plans were implemented by procedures. WAC audits were conducted. Gradually, certification authority was granted to TRU waste generators, in writing. Certification authority could be rescinded if necessary.

The TRU certification program had made some important progress in applying quality requirements to waste management. Program criteria had been established prior to implementation. Items important to quality were specifically identified as activities to which certain controls and/or verifications must be applied. Plans and procedures were written by the implementing group (generators), not an oversight group. On-site program audits were conducted as part of the approved plan. Non-conformances were identified and corrected. Records of all these activities were prepared and maintained. Policy, direction, and oversight were kept seperate from the implementing and verification activities. A formal program had been established, this time in the proper sequence, e.g., guidance preceded the actual activities.

The overall WIPP Certification Program was itself formalized by a Quality Program Plan (QPP). Compliance with the QPP was in turn audited by a seperate DOE QA organization. WIPP WAC audits were conducted in the presence of a representative of the State of New Mexico Environmental Evaluation Group (EEG), who could criticize the quality of the audits, or challenge audit conclusions. There were no major challenges by the EEG, but several of their comments during audits were incorporated into audit findings.

The WIPP-WAC program has been reasonably successful. Can DOE, by adopting the TRU WIPP-WAC program elements, plans and direction, satisfy the requirements of DOE 5820-2 Chapter III? Well, not totally. In fact, there are major issues still to be resolved. The WIPP certification program was not designed to produce what is now considered adequate waste form verification, by specific sample or analysis to demonstrate compliance with all waste form criteria. Even more devastating, the accuracy and precision requirements related to radionuclide type and quantity assessment (assay) have been dramatically modified.

Radiation detection instruments (assay systems) were suddenly required to be more precise; in fact, the new requirements for precision and accuracy may now exceed assay system capabilities. What happened?

Two things happened, both very important, because they begin to stretch the ability to achieve reasonable compliance and begin to come close to requiring "data for data's sake".

First came EPA's RCRA regulations, imposed on mixed waste. These regulations identify the need for waste stream analysis and waste characterization. These requirements were further augmented by the need for "Performance Assessment" first appearing in 40 CFR 191, now also part of DOE 5820-2A, Chapter III. The intent of performance assessment is to determine whether wastes can be safely buried without fear of migration to water, air or the food chain, or release by inadvertant intrusion into an abandoned waste disposal site in the future.

EPA RCRA compliance methods for waste analysis stress representative sampling, a fairly sensible approach, because RCRA is primarily concerned with hazardous liquid wastes. Representative samples of liquid wastes can usually be safely collected and analyzed. The waste analysis process is fundamental to performing risk assessments for waste disposal sites. Hazardous materials in waste are identified and quantified to create a source term, which is dispersed along identified pathways in order to assess risks to receptors. So far, RCRA is fundamentally sound.

However, there are other catagories of RCRA wastes for which there is currently no regulatory consensus on sampling. One example is combustible waste, which includes burnable trash consisting of cloth, paper, and plastics. Another general catagory of RCRA wastes not easily sampled is "hard" waste, e.g., glass, metals, woods, and synthetic woods, contaminated with RCRA listed materials. These wastes constitute a major portion of DOE's mixed wastes.

Communication with RCRA "hot line" specialists leads to the conclusion that EPA does not currently define these wastes, has no established sampling protocols, and has not established treatment standards. Further, unless one were to shred and homogenize these wastes, there is no way to collect a "representative" sample, and no reason to try. The need to further determine chemical composition of wastes already called "hazardous" is highly questionable, because general characteristics are already known.

Presence of radioactive materials makes sampling these wastes even more undesirable, because collection of samples and subsequent analysis must be by methods and in facilities which minimize actual or potential radiation exposure. There are not sufficient sorting and analytical facilities to perform these tasks safely and the need to provide them is not justified in terms of avoided health effects.

The second major requirement which begins to enter the "data for data's sake" category is assay, or assessment of the types and quantities of radioactive materials in low-level or low-level mixed wastes. How good do these assays need to be?

And how much time collecting "representative" samples or performing measurements is necessary to do the job, e.g., define a radiological source term to provide assurance that radiological wastes will not migrate to water, air, or food in concentrations large enough to cause public risks. And to what degree should real risks be imposed on current workers to avoid low probability, overly assessed risks to the public?

TRU waste assay devices are well defined and quite sensitive, but are now not considered good enough to provide the precision needed for compliance with TRUPACT shipping requirements.

Low-level waste assay techniques are, in many cases, not nearly as accurate. In short, how much really needs to be known about wastes in order to dispose of them safely? Or in terms of Quality Assurance and Data Quality Objectives, how good does the data need to be?

Consider the need to characterize waste from a potential migration perspective, and consider what we know about waste characteristics even without actual sampling. Applicable Waste Acceptance Criteria (WAC) in DOE 5820-2A Chapter III prohibit explosives, pyrophorics, reactives, corrosives, pressurized gas cylinders, pathogens, and biological wastes. Prohibiting these materials eliminates highly reactive materials and some gas generators from wastes. Further, there are severe limitations on quantities of liquids, such that liquids can be considered absent. The WAC thus conditions low-level and low-level mixed wastes to be non-reactive and immobile when buried.

The low-level waste certification program, a new DOE 5820-2 Chapter III requirement, will help ensure that wastes to be disposed meet these criteria. Meeting these criteria helps characterize the waste.

However, demonstrating and documenting that precluded waste forms are really absent requires careful consideration, and some sampling, where sampling is feasible. Following is a series of waste certification, waste characterization strategies.

Specific sampling/analysis should be required only for those waste streams which can be reasonably sampled without creating additional radiation exposure problems. Additional knowledge of waste stream composition can be used to further characterize waste. This combined strategy is called "knowledge of process" and is identified as an acceptable technique for mixed waste characterization in a combined EPA/NRC document "Joint EPA/NRC Guidance on the Definition and Identification of Commercial Mixed Low-Level Radioactive and Hazardous Waste", May 2, 1987. It is one of several joint EPA/NRC documents on the subject of mixed waste dual regulation, and it demonstrates a willingness on the part of the two regulatory entities to weigh the need to specifically sample waste streams in light of other regulatory requirements, such as ALARA.

There are liquid low-level and low-level mixed waste streams which are consistent in content and can be reasonably sampled and analyzed for radioactive materials and hazardous waste constituents. These liquid wastes must be treated prior to disposal, but in general, liquid waste stream sampling is a viable method for waste characterization. For inhomogeneous solid wastes, waste characterization can be accomplished by a series of tasks, starting with material balance techniques.

Material balance begins by identifying materials which enter processing or work areas where waste is generated. Types and volumes of materials are identified. Currently existing records or requirements, such as purchase orders, special procedures for control of hazardous materials orders, and materials distribution records are all useful in identifying these materials including radioactive materials which enter process areas. Materials, not hazardous, but contributing to major volumes of waste should also be identified. Chemical processes must be analyzed to see whether different hazardous materials are created. In this way, predictions can be made concerning types and quantities of many different kinds of hazardous, radioactive and non-hazardous materials. This information is useful for waste minimization, characterization, certification, classification, treatment, and, especially Performance Assessment.

Some materials will be consumed by the processes. Some may be released as liquids, which can be sampled. Certain quantities of volatile hazardous materials will be released to, and eventually out of, exhaust air handling systems. Concentrations of these materials can be measured; in fact, they must be measured to determine compliance with 40 CFR 61 (NESHAPS). Certain quantities of hazardous and radioactive materials are incorporated into products. The above sequence therefore identifies types and quantities of materials put into the system, makes evaluations and measurements of materials "lost" from the system due to product, liquid, and airborne removal, and makes reasonable and conservative estimates of types and quantities of residual materials which are present in waste. There should be a limited need to collect additional waste samples, either prior to shipping or upon receipt at the disposal site.

Proper implementation of waste certification programs, with approvals and audits by disposal site representatives, are an acceptable substitute to sampling. The large variety of objects in solid waste containers, contaminated with radioactive and/or hazardous materials, do not allow representative sampling. The combination of materials balance, and sampling/analysis only when practicable, is a systems approach to waste compliance. The same systems approach is applicable to determination of certain difficult to measure radioactive materials in low-level waste. Several types and combinations of radioactive materials in low-level wastes are difficult to impossible to assay. Examples are tritium (in other than liquid form), mixed fission products, carbon-14 and activation products.

Many types of low-level mixed wastes must be treated to comply with DOE and EPA waste disposal requirements. Incineration, shred and grout, and cementation, are examples of acceptable treatment methods. Compaction and absorption are not, at least by EPA standards. Treated low-level and low-level mixed wastes must be characterized and classified also. Acceptable treatment methods in general allow representative sampling, somewhere in the treatment process.

There is a second issue regarding need for sampling of wastes, namely compliance verification. This activity is usually performed at waste disposal sites, and its purpose is to confirm that wastes are properly characterized in terms of type and volume. There are several possible verification techniques.

One method is to open up waste containers as they arrive, examine and sort wastes, or collect samples of wastes. This technique, if applied to low-level or low-level mixed wastes, requires in some cases, construction of facilities which provide adequate worker and environmental protection. Although some sorting and sampling capability is probably required at disposal sites, the capability should be limited, and based on minimal sampling programs for verification.

A second method for verification involves use of non-destructive examination techniques such as real time radiography (RTR) to examine wastes without opening waste packages. RTR is an excellent tool for detecting presence of liquids, pressurized containers, odd-shapes and odd-item identification, and certain waste forms such as monolithic wastes (soil, sludge, or cement) combustibles, metals and ceramics. The TRU program has proven conclusively that RTR is a valuable verification tool, which gets more valuable as operator capabilities improve with practice.

When waste generators in the TRU program had their own violation shown to them on RTR video tapes, and were made to rectify their mistakes at their own expense, the numbers of violations were quickly reduced. Just the knowledge that an x-ray unit was going to examine waste packages helped reduce the number of waste form violations in the TRU waste program. All low-level or low-level mixed waste disposal sites should consider using the RTR. The TRU program has a mobile RTR unit, which can examine waste containers of all sizes, and is available for on-site use. Currently, the DOE mobile RTR is being under-utilized. It could be used on low-level waste.

A third waste verification method is to implement the certification program described earlier in this paper. Waste disposal site operators review and approve certification plans, review implementing procedures and perform audits to assess generator compliance with provisions of the plans and procedures. The onus for compliance, including waste characterization and classification, is placed on the generator organization. A well-managed certification program can reduce the need for disposal site sampling activities. A carefully designed waste management program, combining waste sampling and analysis (where feasible) and "knowledge of process" (where sampling is prohibitive or conflicts with health and safety criteria), at the generator site, together with a verification program with limited RTR and sorting/sampling capability at the disposal site can result in an effective waste compliance program, without total reliance on waste sampling.

In summary, imposition of new EPA and DOE requirements on low-level and low-level mixed waste management activities has caused substantial impacts. Some of the new requirements are easy to accommodate; others are not. Combining DOE and EPA requirements for low-level and low-level mixed waste management can, in general, be accommodated, but in some cases alternative compliance methods are required. There is a need for interpretation and analysis of regulations, and development of practical compliance methods, which are not always based on literal regulatory interpretation. Existing EPA/NRC documents on mixed wastes have established precedents for this approach.

WASTE CERTIFICATION: WHO REALLY IS ON FIRST?

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INTRODUCTION

Waste certification is the process of stating whether or not a given waste package meets the acceptance criteria of whatever facility is receiving the package. Establishing a program for certification of low-level waste requires coordination of a variety of requirements and limitations, including regulations, physical characteristics of the waste and of the type of radiation emitted by radionuclides in the waste, uncertainty in measurements, quality assurance, and personnel exposures. The goal of such a program must be to provide an acceptable degree of assurance that the waste generating facility will be able to convince the waste receiving facility that individual waste packages do meet the applicable waste acceptance criteria.

The preceding paragraph raises many questions: what is an "acceptable degree of assurance"? What does one have to do to "convince" a receiving facility? How can the measurement uncertainty be taken into account? This paper attempts to address several of those questions in the context of the development being done in the solid low-level waste (SLLW) certification program at the Oak Ridge National Laboratory (ORNL). First, a brief history of the SLLW certification program at ORNL is presented. The remaining discussions are devoted to considering the problems and pitfalls of implementing a waste certification program, concentrating on such areas as the responsibilities of various organizations and individuals, waste characterization techniques, handling levels of uncertainty, and development of waste acceptance criteria.

SOLID LOW-LEVEL WASTE CERTIFICATION AT ORNL

SLLW certification began in earnest at ORNL in April 1986 when SLLW disposal operations in Solid Waste Storage Area (SWSA) 6 at ORNL were halted by order of the Department of Energy (DOE) Oak Ridge Operations Office (ORO). The order was issued because hazardous wastes were being disposed in SWSA 6 in violation of the Resource Conservation and Recovery Act (RCRA). A SLLW certification program was instituted to improve the segregation of hazardous waste from SLLW and to provide assurance that the wastes were being managed properly. The certification program includes:

- improved training for operators and supervisors in areas generating SLLW, with restrictions against untrained personnel being allow to package SLLW
- documentation to track the individual waste packets being placed into the SLLW container
- SLLW generator program reviews by the Waste Disposal Coordinator
- verification of appropriate SLLW packaging by real-time radiography (RTR)

[Reference 1]

In addition to being segregated from hazardous and nonradioactive wastes, SLLW is also sorted into categories based on the level of radiation hazard present and, in a few cases, on the type of material present in the waste, such as for contaminated asbestos. Under the present system, the categorization is dependent on the external radiation levels measured at the surface of each disposal container. [Reference 2]

Under DOE Order 5820.2A, issued September 26, 1988, [Reference 3], radioactive waste management facilities must be designed to meet dose based performance objectives. An integral part of waste management strategy is the development of a SLLW classification system designed to accommodate those performance objectives. While several parameters, such as the physical characteristics of the waste packages and the disposal site, determine the specific classification, the basis for SLLW characterization and certification is determining the concentration of radionuclides in the waste either through direct measurement methods or through indirect methods. This approach contrasts the classification scheme based on external radiation hazard and estimated radionuclide concentrations.

Due to the evolution of a more rigorous radionuclide concentration based classification system for management of SLLW, redirection of the ORNL SLLW certification program is needed to provide the necessary waste characterization. However, the nature and character of the waste streams at ORNL are such that completely reliable, reproducible characterization is not always possible. The development of the SLLW certification strategy and the implementation of the modified program will have to account for the numerous uncertainties involved. This paper discussed some of the uncertainties and possible means of addressing them.

WASTE CHARACTERIZATION

The most important part of the SLLW certification program based on radionuclide concentration limits is characterizing waste streams. In addition to characterization of waste according to its radionuclide content, this part of the program must also provide assurance that prohibited constituents are being excluded. Table 1 includes a list of several items which are to be excluded from ORNL SLLW, based on current and draft waste acceptance criteria. Additional items may be included on the prohibition list as the waste acceptance criteria for new treatment, storage, and disposal facilities are developed.

Table 1. Items Prohibited from Solid Low-Level Waste

Based on current and proposed waste acceptance criteria for disposal sites on the Oak Ridge Reservation, the following articles and material are not allowed in SLLW generated at ORNL.

- free liquids
- oils and oily wastes
- PCB contaminated materials
- pesticides (herbicides, insecticides, etc.)
- compressed gases
- hazardous waste as defined in the Resource Conservation and Recovery Act
    - arsenic
    - barium
    - cadmium
    - chromium
    - lead
    - mercury
    - selenium
    - silver
    - toxicity characteristic compounds
    - ignitable waste
    - reactive waste
    - corrosive waste
    - cyanide or sulfur bearing waste
- pyrophoric materials
- chelating agents in excess of 0.1% by weight
- respirable particles in excess of 1% by weight
- pathogenic, infectious, toxic, or poisonous materials
- explosive materials

GENERAL METHODS OF WASTE CHARACTERIZATION

According to guidance given by the Nuclear Regulatory Commission (NRC) [Reference 4] and reinforced by DOE [Reference 3], the acceptable techniques for characterizing wastes are:

1. Measurement

Either direct or indirect measurement may be used. Direct measurement would include techniques such as gamma spectroscopy on waste packets or waste packages or sampling the waste stream. Indirect methods may include using gross measurements, such as surface exposure rates, in conjunction with scaling factors. The indirect methods would be applicable to a well defined waste stream and would have to be substantiated through use of direct measurement techniques.

2. Material Accountability

Essentially a bookkeeping method, accountability uses the difference between material input for a process and the amount of that material that is present in the product, including the amounts known to be consumed or converted in the process and the quantity remaining as contamination on surfaces or inside pipes and ducts. To be used as a basis for waste characterization, material accountability would have to be substantiated through direct measurement techniques.

3. Process Knowledge

Through an understanding of the material input to a process and the manner in which the material is manipulated or handled, the waste may be characterized by use of a model which accounts for the quantities which will be included in the waste from that process. The model may be rather simple or complex, depending on the process involved, but also must be substantiated.

PROCEDURE FOR CHARACTERIZING WASTE

Waste characterization is, initially, the responsibility of the waste generator, with guidance and assistance from the waste operations and certification groups. While the final characterization technique for a specific waste generator will be dependent on the process generating waste, the approach to developing characterization data will be a phased process.

Phase I - Gross Characterization

The initial information for SLLW characterization describes the gross character of specific waste streams. This information may be gathered through review of previously collected data, including the radioactive waste data base system, or through questionnaires and interviews with waste generators. Phase I consists of two actions:

1. Identify and categorize the waste stream

Identification of the waste stream may be the building, process, or any other label which will readily identify the waste generator and will be specific to a particular waste stream. At this point, categorization of the waste stream consists of sorting the process into the broad categories: homogeneous or heterogeneous with respect to the physical composition, consistent or inconsistent over time with respect to the constituency and concentration, and generated as a result of routine operation or from a specific campaign.

Homogeneity or heterogeneity of the waste physical form is based on the gross characteristics of a "typical" waste package generated through that process. While there will never be any waste package that is completely homogeneous, in that small discontinuities exist in any physical field, the waste should be categorized according to the degree of difficulty involved in obtaining a representative sample of the waste. For example, a container of miscellaneous, unconsolidated trash such as clothing, paper, and plastic would be considered heterogeneous, while a more uniform material such as contaminated soil could be considered homogeneous, since a representative sample of the former would be difficult, if not impossible, to obtain, but would be relatively easily done from the latter.

The consistency or inconsistency in the composition of a waste stream may also be considered in the context of the difficulty in obtaining a representative sample of the waste stream. If a routine sampling program were to be established for the waste stream in question, the degree of consistency would be directly tied to the frequency with which samples would have to be collected in order to be representative. For example, a waste stream that routinely has a wide variation in the type and quantity of material present, such that samples would have to be collected on a weekly, or more often, basis in order to be representative, would be considered inconsistent. However, a waste stream that does not have as great a variation, such that annual samples would be adequately representative, would be considered consistent.

The distinction between operational waste generation and waste generated from a specific campaign is related to the length of time the generating process is in operation. Short term projects would be considered campaigns, and processes that will continue for longer terms would be considered operational.

Therefore, the result of this phase of waste characterization would be to group each waste stream into one of the following categories:

a. homogeneous form, consistent composition, operationally generated
b. homogeneous form, inconsistent composition, operationally generated
c. homogeneous form, inconsistent composition, generated in campaign
d. heterogeneous form, consistent composition, operationally generated
e. heterogeneous form, inconsistent composition, operationally generated
f. heterogeneous form, inconsistent composition, generated in campaign

2. Determine the possible constituency of the waste stream

Each SLLW generator must develop a process flow diagram to describe the type and quantity of various material that may be present in SLLW generated through that process. The flow diagram will show the input material for the process, material which may be created through the process, and the portion of that which may be present in the SLLW generated by the process, including supplies and equipment used for cleaning and decontamination. For example, an analytical chemistry laboratory process flow diagram would show the various chemicals that are used in the analytical procedure, the changes that occur in chemical composition as a result of the analytical process itself, and the type and approximate quantity of those materials that may be present in the waste stream. For the initial phase of waste characterization, the quantitation would not need to be rigorous, but would be designed to show what material will constitute the major portion of the waste and which will be present in only trace quantities. The emphasis in developing such a flow diagram is to identify those prohibited constituents that may be present in the waste, but that can be eliminated through administrative and process controls.

Phase II - Establish Baseline Characterization

After obtaining the gross information from Phase I, a thorough sampling and analysis campaign will be instituted to determine the baseline SLLW characterization data, with the purpose of developing routine procedures for certifying the waste at the generator level. The specific parameters to be included in this sampling campaign will be decided for each waste stream, based on the information provided in the gross characterization study, with the type and quantity of samples dependent on the categorization data. For example, a SLLW stream that is homogeneous, consistent, and operationally generated should be sampled more thoroughly than a heterogenous, inconsistent, campaign waste stream, since the data will be of more use in establishing routine certification procedures in the former than in the latter.

Phase III - Implement Routine Characterization Program

With the baseline established, a routine program for obtaining waste characterization data must be developed for each SLLW generator. The specific procedures will be dependent on the individual waste stream involved, but must be one of the three techniques listed earlier in this section. In all cases, the individual technique must be substantiated to provide the necessary confidence level for certification. In addition to the objective data on the waste stream categorization and baseline analyses, the following criteria must also be considered in establishing a routine characterization program:

1. Personnel exposures

Prior to implementing a routine program, the personnel exposures which may result from characterization activities such as sampling and analysis must be evaluated. If the expected personnel exposures are unacceptably high, a different characterization technique should be used in accordance with the ORNL commitment to maintain exposures as low as reasonably achievable (ALARA). [Reference 5]

2. Available technology

In some cases, instrumentation and monitoring techniques which can be applied to waste characterization may be commercially available. However, for some waste streams, such as those involving the production of radionuclides having only weak beta emissions (e.g., tritium), characterization through direct or indirect measurement may not be possible.

3. Cost

The cost of providing complete waste characterization data must be balanced against the consequences of not having the information available. For example, an operation that generates only a small amount of SLLW will not be able to offset the expense of instruments needed to completely characterize the waste stream.

One approach to dealing with the impediments to complete waste characterization posed by limiting personnel exposure and by cost-benefit analysis is to establish "regional" SLLW characterization facilities to provide measurement capability to a group of generators. The viability of such an approach will be dependent on the type and quantity of SLLW being generated, and can be evaluated more thoroughly after the Phase I and Phase II studies described above.

As should begin to be evident from the above discussions, waste certification is a deterministic process, in that waste either does or does not meet the appropriate acceptance criteria. The levels of uncertainty associated with characterization of the waste, which would be considered a probabilistic process, must be considered when certifying that a given waste package meets a specific set of criteria. However, the act of certifying the waste does not have reported uncertainty associated with it. Therefore, some consideration of the necessary uncertainty or confidence level must enter into the characterization process.

LEVELS OF UNCERTAINTY

The manner in which uncertainties are expressed can have a significant impact on the development of waste characterization programs. One expression of uncertainty that is generally familiar is the confidence level, or confidence interval. Simply stated, the confidence interval is the probability, expressed as a percentage, that the true mean value for a set of measurements falls within the computed uncertainty interval about the calculated average. Therefore, if the arithmetic average of a series of measurements is expressed as 50 ± 10 at the 95% confidence level, that means that there is 95% confidence that the true mean value lies within the range of 40 to 60. Applying this definition to determining the characteristics of a waste shipment can lead to some difficulties. Although the confidence level is an important parameter to be considered in any type of quantitative analysis, other factors may preclude such an expression being adopted without some modification.

To take an example of a waste shipment, assume that n representative samples of the waste batch are taken and analyzed. The τ (* 100%) confidence interval for the results would be expressed as:

$$\bar{x} \pm z_c(n-1,\ (1-\tau)\ /\ 2)\ *\ S\ /\ \sqrt{n}$$

where z_c is the statistical uncertainty as a function of the number of samples and the selected confidence level and S is the standard deviation of the measurements. [Reference 6]

To demonstrate the application of this approach, assume that two samples are collected and show results 20 and 30 ppm, giving a mean of 25 ppm and a standard deviation of 7.07 ppm. The 95% confidence interval would be 25 ± 64 ppm. This shows that, while it is possible to attain a 95% confidence level with only two samples, the associated interval of uncertainty is approximately 250% of the calculated average value.

The stated range of uncertainty can be reduced by either collecting more samples, since the interval is dependent on n-1, or by reducing the required confidence level. Using the same two samples in the above example, the 80% confidence interval would be 25 ± 15 ppm. This reduces the interval to approximately 60% of the mean value. Conversely, if the number of samples were to be increased to 25, with the calculated mean still at 25 ppm and standard deviation at 7.07 ppm, the 95% confidence interval would be 25 ± 3 ppm.

Therefore, if the confidence level is to be the determinant for sampling and characterization of a waste shipment, the viable options, in order to have a useful procedure, are to (1) establish a high confidence level (e.g., 95%), but collect only a few samples, leaving a large interval of uncertainty about the mean value, (2) establish a relatively low confidence level (e.g., 75%), collect only a few samples, leaving a fairly large, but acceptable interval of uncertainty, or (3) establish a high confidence level, and collect several samples, leaving a small interval of uncertainty. None of these options are particularly attractive. Under the first, reporting values with an uncertainty of more than 200% does not provide the assurance that waste certification should provide. Similarly, establishing a low confidence level may not provide adequate assurance and may not be acceptable to regulatory agencies. The inordinate cost associated with sampling and analysis makes the third option economically unjustifiable.

A different approach to establishing confidence would be to establish a statistical tolerance bound for a waste shipment. [Reference 7] A tolerance bound would establish an upper limit on the uncertainty associated with a series of measurements. In practice, the statistical tolerance bound for a series of n samples would be:

$$\bar{x} \pm k(n,p) * S$$

where k is the τ/p tolerance bound for the series with standard deviation S, meaning that there is a τ (*100%) confidence that at least p (*100%) of the sample results are less than the tolerance bound.

Using the same example of two samples with a calculated mean of 25 ppm and standard deviation of 7.07 ppm, the 95/95 tolerance bound for the series would be 25 ± 186 ppm. This again creates a large uncertainty interval about the mean if a high tolerance bound is desired with only a few samples. The 75/95 tolerance bound for the series (75% confidence that 95% are below the limit), would be 25 ± 36. For n = 25, the 95/95 tolerance bound would be 25 ± 16.

While the uncertainty intervals for this approach are still larger than desired, the advantage to using the tolerance bound is that samples of previous waste shipments from the same waste generating process can be included in the calculation of tolerance bounds. If n samples are collected from the current shipment and combined with m samples from the previous shipments, the tolerance bound is then:

$$\bar{x} \pm k(n+m,p) * S$$

This method of calculating uncertainty can then effectively combine samples from several waste shipments, giving the advantage of lowering the interval of uncertainty as though additional samples had been collected.

However, there are stringent limitations to applying this technique. The process generating the waste must meet the following three conditions in order to be able to establish a cumulative tolerance bound for waste shipments:

1. the initial characterization of the waste stream must have been done through a statistically valid sampling program

2. process and administrative controls that are established for the waste generating process must maintain control of the process within statistical limits

3. the waste generating process must be in a steady-state operation, in that no significant variation has occurred which would alter the waste characterization

These conditions are not easily met in many instances, particularly at a research facility such as a national laboratory. However, as long as such conditions can be met, the use of a statistical tolerance bound provides definite advantages to strictly using confidence levels in waste characterization.

There are activities other than increased sampling that can improve the confidence in waste characterization. Similar to the theory behind using statistical tolerance bounds, an accumulated confidence level can be used to provide uncertainty estimates. The accumulated confidence interval is the estimated of uncertainty in waste characterization based on the control, documentation, and verification of the process which generates the waste as opposed to being based solely on the analysis of samples from the waste stream.

Under this approach, subjective data would contribute to the confidence level of waste characterization. The generator certification process, including administrative and process controls, adequacy of documentation, and performance on audits and reviews, increases the reliability of waste characterization data. At this point, the development of a waste certification program which accounts for the idiosyncracies of individual waste generating processes becomes critical. The combination of the objective data obtained through measurements in the waste characterization process with the subjective evaluation of the reliability of process knowledge that comprises the remainder of waste characterization data is what will enable the waste generator to certify, with adequate assurance, that the waste being transferred to another facility does meet the acceptance criteria of that facility.

Improving statistical surety depends on the development and documentation of a rigorous certification program with clearly defined responsibilities and duties. The following section discusses, in general terms, how such a program should be designed.

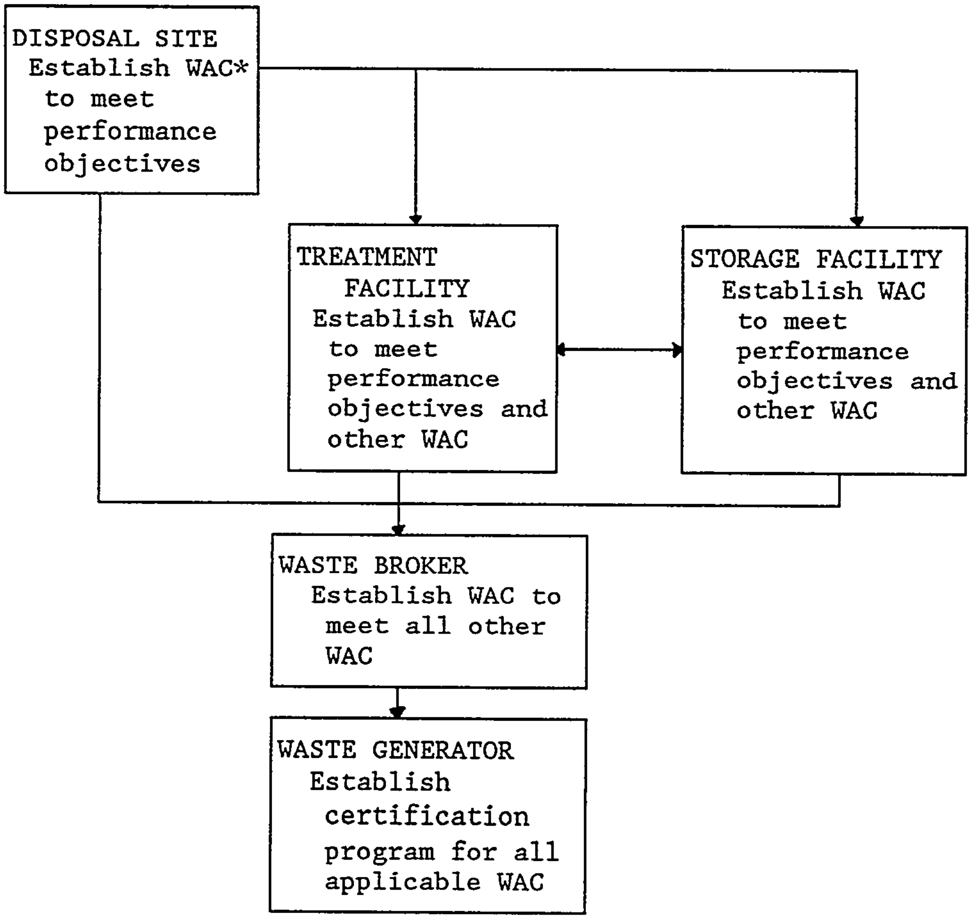
WASTE ACCEPTANCE CRITERIA

As defined in the introduction, waste certification is the process of stating whether or not a given waste package meets the acceptance criteria of whatever facility is receiving the package. From that definition, the obvious first requirement in establishing a waste certification program is to have a set of acceptance criteria against which to certify the wastes. While obvious, this step is often neglected in trying to define the requirements in certification programs - an attempt is made to "certify" waste without knowing the limitations or restrictions that will be placed on the waste in terms of physical, chemical, or radiological characteristics. Such an auspicious beginning is sure to create frustration and fail to create a coherent waste certification program.

Under DOE Order 5820.2A, solid low-level waste disposal sites are to be designed and operated to meet specified performance objectives. The Order states those performance objectives in terms of the permissible effective dose equivalent rate for nearby residents. This is similar to the approach taken in commercial nuclear facility regulation, where an allowable population or individual dose is assigned and specific criteria and restrictions are assigned to the facility based on the capability of meeting the dose limit. Low-level waste disposal sites are required to establish a set of restrictions and criteria that must be met by the waste emplaced at the site in order to ensure that the performance objectives are not violated. These limitations and definitions are what this paper refers to as "waste acceptance criteria".

Figure 1 depicts a flow chart of the development of waste acceptance criteria. The following paragraphs discuss the considerations that enter into creating the criteria. Later discussions deal with the development of certification programs to address compliance with the criteria.

Development of criteria for a given disposal site will generally entail assessment of the possible radiation exposure pathways from waste at the site. Many of the criteria will be dependent on the assumptions made in performing the exposure pathway evaluation. For example, assumptions regarding the structural stability of the waste form may result in acceptance criteria that limit the acceptability of compressible, biodegradable, or other less stable waste forms. Whatever the limitations imposed in the criteria may be, the primary point for the purposes of this paper, as far as developing a waste certification program is concerned, is that the disposal site must establish waste acceptance criteria which ensure that the site will meet the applicable performance objectives.



* WAC = Waste Acceptance Criteria

Figure 1. Waste Acceptance Criteria Development Flow Chart

Wastes being placed into interim or temporary storage facilities, whether long or short term, must be certified as meeting the disposal site waste acceptance criteria at the time the stored wastes are removed from storage and sent to disposal. Therefore, it would be prudent to impose acceptance criteria for the storage facility that will ensure that the wastes will meet the criteria upon removal. In addition, storage facilities are subject to the performance criteria requirements of DOE Order 5820.2A. Because of this, there may be additional limitations on acceptance of waste at the storage facility that may not be present for the disposal facility. This is a second set of waste acceptance criteria that will need to be considered in developing a certification program.

Similar to the storage facility, waste treatment facilities will also be required to develop waste acceptance criteria that no only ensures that the facility will meet the prescribed performance objectives, but also that the waste will meet the acceptance criteria for other treatment, storage, or disposal facilities after it has been processed. Development of these criteria will require an evaluation of the form in which the waste must be in order to meet the acceptance criteria at sites to where it will be shipped. Starting from that form and working backward, the perturbations to the required form resulting from the treatment process will dictate the acceptance criteria for the facility.

If a waste broker is used, as is the case for most commercial operations, the acceptance criteria for the broker to assume possession of waste must also account for the limitations that will be imposed be acceptance criteria at any of the facilities to where the waste may be shipped. Inclusion of a waste broker into the waste management process somewhat simplifies the certification program at the generator facility. Rather than having to accommodate the several sets of waste acceptance criteria for each different facility, a waste broker assumes the responsibility of accommodating all the other criteria and presents a single set of acceptance criteria to the generator. At ORNL, an internal organization within the waste management operations organization performs as a waste broker would in the commercial sector. However, additional brokering may also be necessary.

WASTE CERTIFICATION PROCESS

Figure 2 shows a flow diagram of the waste certification process. The process is essentially an inverse of the waste acceptance criteria flow chart of Figure 1, in that the certification process begins at the generator and proceeds to the disposal site, while the earlier discussion began with the disposal criteria and developed to the generator.

The certification process begins at the point of generation. As the waste generator characterizes the waste stream by the methods outlined earlier, additional feedback to the generating process can be provided in the form of administrative or engineering controls that would facilitate waste characterization. Improving or increasing the controls on the process generating radioactive waste can provide additional surety to the characterization process. As simple a procedure as placing the hazardous waste receptacles on the opposite side of the room from the radioactive waste containers can improve the accumulated confidence level of the waste certification program.

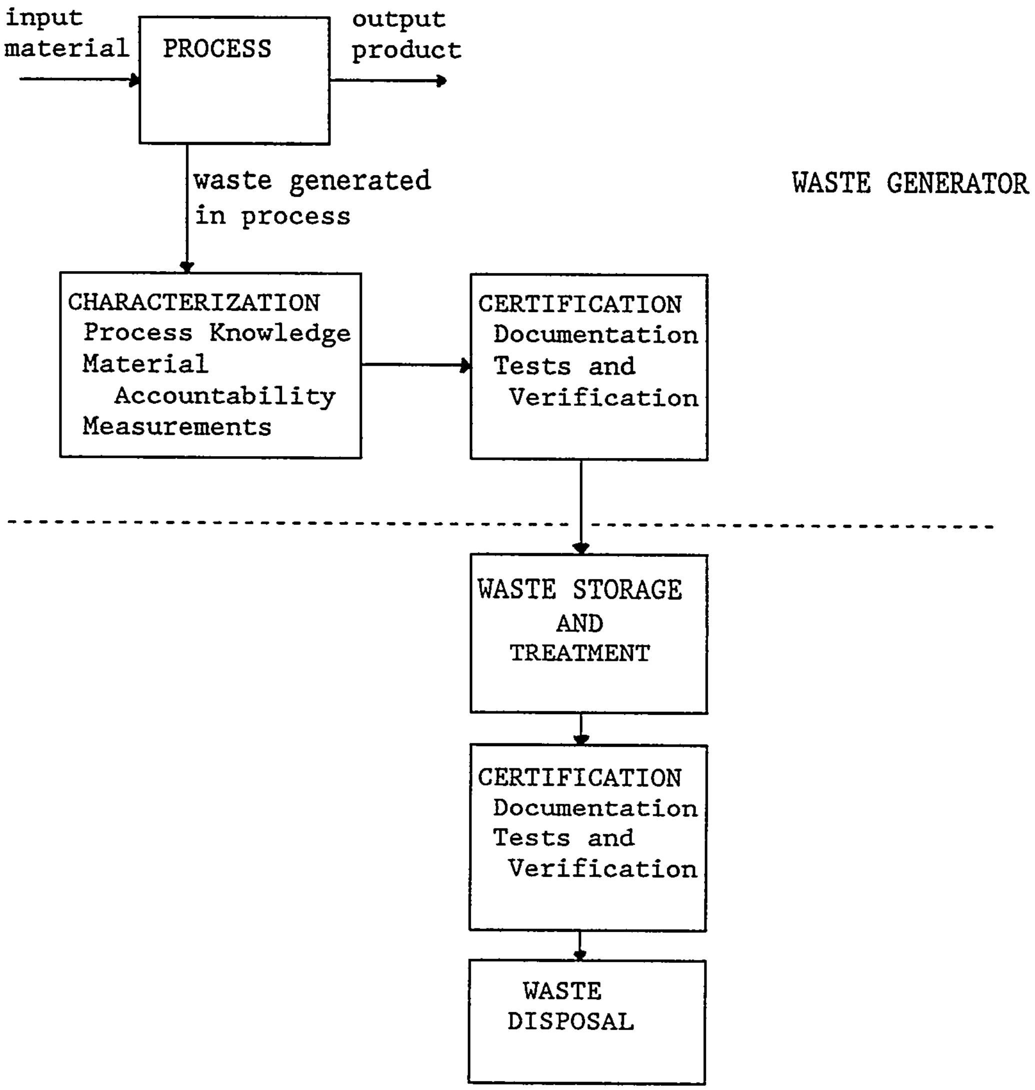


Figure 2. Waste Certification Process Flow Chart

As shown in Figure 2, the waste is characterized by the waste generator at the point of generation. With an adequate characterization, the waste is certified against the applicable waste acceptance criteria. The certification process may be the responsibility of the generator, but is normally a multiple stage approach that includes the waste broker and other organizations. At ORNL, the waste generator must certify that the generated waste meets the criteria for transferring the containers to the waste operations group, which serves in the capacity of a waste broker for the numerous radioactive waste generators across ORNL. The waste operations organization adds to the documentation that the generator provides by performing additional tests, such as real-time radiographic examinations, to verify that the waste containers meet the acceptance criteria for treatment, storage, or disposal.

Waste certification, then, is a progression. Each organization that assumes possession of a waste container must certify that the container meets the acceptance criteria of the next organization to whom possession will be transferred. In turn, each organization to whom the waste container is transferred has the right and the responsibility to audit the entire sequence up to that point. For example, the waste generator certifies that the waste meets the acceptance criteria of the waste broker. The broker must review the generator's program to ensure that the certification is valid. When the broker transfers the waste to a treatment facility, that facility should audit the broker's certification program as well as that of the original waste generator. This process continues until ultimate disposal of the waste. The disposal site must have the right to audit any organization that has ever had possession of the waste container.

CONCLUSION

Waste certification is seen as a multiple phase approach to determining that a given waste container meets the waste acceptance criteria being imposed by treatment, storage, disposal, or other waste management facilities. The certification process must begin at the waste generator, who has the responsibility to characterize the waste. Waste characterization, performed through material accountability, process knowledge, or physical measurements, is a determination of the chemical, physical, and radiological properties of the waste and is a probabilistic method. However, waste certification, which is the act of stating that the waste does meet the applicable criteria, is a deterministic process. The development of a certification program must address the levels of confidence in waste characterization and the means to improve reliability.

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WASTE CHARACTERIZATION: WHAT'S ON SECOND?

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INTRODUCTION

Waste characterization is the process whereby the physical properties and chemical composition of waste are determined. Waste characterization is an important element of a waste certification program in that it provides information which is necessary to certify that waste meets the acceptance criteria for storage, treatment, or disposal. Department of Energy (DOE) Order 5820.2A and WIPP-DOE-069 list and describe the germane waste form, package, and container criteria for the storage of both solid low-level waste (SLLW) and transuranic (TRU) waste, including chemical composition and compatibility, hazardous material content (e.g., lead), fissile material content, radioisotopic inventory, particulate content, equivalent alpha activity, thermal heat output, and absence of free liquids, explosives, and compressed gases.

At the Oak Ridge National Laboratory (ORNL), the responsibility for waste characterization begins with the individual or individuals who generate the waste. The generator must be able to document the type and estimate the quantity of various materials (e.g., waste forms - physical characteristics -, chemical composition, hazardous materials, major radioisotopes) which have been placed into the waste container. Analyses of process flow sheets and a statistically valid sampling program can provide much of the required information as well as a documented level of confidence in the acquired data. A program is being instituted in which major generator facilities perform radionuclide assay of small packets of waste prior to being placed into a waste drum.

Prior to removing a filled waste drum from a generator facility, an inspection of the container, documentation, and related items is performed. Table 1 presents a summary of the items reviewed. After the inspection, the waste containers are transferred to a central waste certification facility, the Waste Examination Assay Facility (WEAF). The WEAF serves both to verify a portion of the generator's waste characterization data, such as the radioisotope inventory and absence of free liquids and compressed gases, and to perform certain other characterization measurements, such as fissile content and thermal heat output.

WASTE CHARACTERIZATION AT THE GENERATOR FACILITY

The process of characterizing wastes must begin at the point where waste is generated. In order to certify that a given waste package meets the applicable waste acceptance criteria for whatever treatment, storage, or disposal facility that is accepting the waste, the process in which the waste is generated must be examined.

Table 1. Checklist Items for Use at Drum Pick-Up

a. Radiation tag (UCN-2785) attached and properly filled out.

b. Documentation complete (UCN-2822), log-in sheet, accountability transfer form, if required.

c. Check for physical damage (visual).

d. Bolt ring and gasket properly installed and in place.

e. Closure bolt torqued to 45 ft-lbs.

f. Jam nut in proper location and tight.

g. Drum checked to be 17-H.

h. Bar code installed and in place.

In addition to characterization of waste according to its radionuclide content, the waste generator must also provide assurance that constituents which are prohibited by the waste acceptance criteria are being excluded. Table 2 shows a list of several items which must be excluded from SLLW, based on current and draft waste acceptance criteria for the Oak Ridge Reservation. Additional items may be included on the prohibition list as the waste acceptance criteria for new treatment, storage, and disposal facilities are developed.

According to guidance given by the Nuclear Regulatory Commission (NRC) and reinforced in DOE Order 5820.2A, the acceptable techniques for characterizing wastes are:

1. Direct or indirect measurement. Direct measurement would include techniques such as gamma spectroscopy or sampling the waste stream. Indirect methods may include using gross measurements, such as surface exposure rates, in conjunction with scaling factors. The indirect methods would be applicable to a well defined waste stream and would have to be substantiated through use of direct measurement techniques.

2. Material accountability. Essentially a bookkeeping method, accountability uses the difference between material input for a process and the amount of that material that is present in the product, including the amounts known to be consumed or converted in the process and the quantity remaining as contamination on surfaces or inside pipes and ducts. To be used as a basis for waste characterization, material accountability would have to be substantiated through direct measurement techniques.

Table 2. Constituents Prohibited from Solid Low-Level Waste

- free liquids
- oils and oily wastes
- PCB contaminated materials
- pesticides (herbicides, insecticides, etc.)
- compressed gases
- hazardous waste as defined in RCRA
    - arsenic
    - barium
    - cadmium
    - chromium
    - lead
    - mercury
    - selenium
    - silver
    - toxicity characteristic compounds
    - ignitable waste
    - reactive waste
    - corrosive waste
    - cyanide or sulfur bearing waste
- pyrophoric materials
- chelating agents in excess of 0.1% by weight
- respirable particles in excess of 1% by weight
- pathogenic, infectious, toxic, or poisonous materials
- explosive materials

3. Process knowledge. Through an understanding of the material input to a process and the manner in which the material is manipulated or handled, the waste may be characterized by use of a model which accounts for the quantities which will be included in the waste from that process. The model may be rather simple or complex, depending on the process involved, but also must be substantiated.

At ORNL, a study project is being conducted on one of the major low-level waste (LLW) streams to develop a measurement procedure to segregate uncontaminated waste from LLW and to determine the concentration of beta and gamma emitting radionulcides in the waste. The first step in the procedure is the segregation of waste streams.

At the facility, there are several waste streams contaminated with radionuclides that emit only weak beta particles, such as ^{3}H. The procedure being developed is not designed to detect these weak beta emissions. Therefore, the initial stage of the process must be to segregate those waste streams from the streams that can be used in the demonstration project. To accomplish this, a series of administrative controls and controls on the waste generating processes are being instituted to ensure that the streams do not become commingled.

After separating the beta-gamma emitters from the unsuitable wastes, the material will be screened for radioactivity in an instrument called a Waste Curie Monitor. This device consists of a small cabinet lined on four sides with sheets of plastic scintillator material. A plastic bag containing the waste to be monitored is placed inside the cabinet, the door is closed, and a short count (on the order of a few minutes) is made. The plastic scintillators provide an integrated count of all the gamma and hard beta emissions from the waste. Provided the lower limits of detection are chosen appropriately, this screening step will indicate whether or not the waste is contaminated. Since the current operation of this generator facility assumes that all wastes coming from the process area is contaminated, using this instrument should be able to reduce the amount of waste that must be handled as radioactive.

If the waste is contaminated, further analysis will be performed. For gamma emitting nuclides, a germanium-based gamma spectrometry instrument will be used to quantify the radionuclides in the waste. For the radionuclides that emit only beta particles, the waste streams have been chosen so that a defined ratio exists between the quantity of pure beta and beta-gamma emitters. By periodically verifying the ratio, the concentration of all radionuclides in this particular waste stream can be determined through this procedure.

Other characterization methods used by waste generators rely heavily on process knowledge to estimate the quantity of radionuclides in the waste. Although the application of process knowledge to waste characterization involves subjective evaluation, the estimates and procedures for performing the estimates are well documented. Each small package of LLW placed into a waste container is recorded on a log sheet maintained by the generator. The log description of the waste packet includes the date generated, the person placing the waste in the container, estimates of the radionuclide content, physical measurement of the surface radiation levels, and a general description of the waste form. By maintaining this running documentation for each container, the contents are more easily characterized than would be possible by examination of the bulk form.

Additional documentation is prepared when the waste generator needs to transfer the container. A Request for Disposal form is prepared which summarizes and totals the information contained on the individual log records. Both the Request for Disposal and the log sheets are a part of the documentation which accompanies the waste container to assay, treatment, storage, and disposal facilities. Further characterization is performed at the central facilities.

WASTE CHARACTERIZATION SAMPLING PROGRAM

A significant quantity of solid contact-handled transuranic (CH-TRU) and LLW packaged in 208 l (55 gallon) drums is stored at ORNL. The characterization data available for many of these drums was obtained under different criteria and procedures than are now in force. Therefore, some of the data needed to certify the wastes against the appropriate acceptance criteria either do not exist, or do not provide sufficient accuracy, precision, and level of detail. ORNL has not yet instituted a formal waste characterization sampling program for these drums. However, a CH-TRU waste drum sampling program was conceived in the early 1980's to be used as an independent validation of the passive/active neutron (PAN) assay measurements made at the WEAF. [References 1 and 2]

Under the sampling plan, a glove box facility was constructed to obtain samples from selected CH-TRU waste drums. The contents of the drums would be emptied into a glove box and segregated into four categories: cellulose, plastics, glass and ceramics, and metals. Each type of material, excluding metals, would be weighed and homogenized. A specified number of samples, approximately 100 per drum, of different waste types, designated by "content codes" (e.g., decontamination debris, contaminated equipment, dry solids) would be collected and transferred out of the glove box. The collected samples would then be assayed by gamma-ray spectrometry and the results compared to the PAN assay measurements. The proportion of agreement between the matched observations would form the basis for validation of the neutron assay technique.

The statistical sampling program would begin by obtaining a stratified random sample of drums. (Number of drums = n) The variance of the proportion of agreement would also be estimated. The question remaining is how large should n be? The probability that the absolute difference between the estimate of proportion of agreement and the true proportion of agreement is greater than or equal to an arbitrary factor supplied by the experimenter is given by the following equation:

$$\Pr (P-P \geq d) = \text{alpha}$$

Alpha represents the confidence interval, 100 * (1-alpha)% (e.g., alpha = 0.01 corresponds to a 99 percent confidence interval), while d represents the proportion of agreement sought by the experimenter (e.g., for d = 0.2, the experimenter seeks a relative difference between the two measurements of 20 percent).

For example, with a choice of alpha = 0.05 and d = 0.08, 150 drums out of a population of 1,800 would be destructively sampled. There are not sufficient numbers of drums in certain waste content codes for a statistically valid program. Consequently, all drums within that waste content code were to be sampled. Other content codes encompass a large number of drums. A stratified random sample of these drums at the generator sites was chosen to ensure that a wide range of drum activity concentrations would be included in the sample. The strata limits were determined by the cumulative square root of the frequency method [Reference 1].

The number of samples to be collected from each waste category (i.e., metals, plastics, cellulosics, glass and ceramics) within a selected drum is based upon the width of the confidence interval desired, determined by the size of the difference between the assay measurement results for the two methods which would be considered significant. The values of proportion, by weight, of the waste categories in the drum and the variance of the activity concentration distribution of an isotope within a waste category could be estimated from a pilot sample.

The observations from the destructive and nondestructive assay can then be used to determine if the nondestructive assay (NDA) method provides accurate estimates of the mean concentration of the isotopes present in the waste container. At this time, the sampling program has not been instituted at ORNL.

CENTRAL WASTE CERTIFICATION FACILITY

The ORNL central waste certification facility is the WEAF, Building 7824, located in Solid Waste Storage Area (SWSA) 5. It was established in 1982 as the ORNL central certification facility for the NDA and nondestructive examination (NDE) of CH-TRU waste. In November of 1984, an NDE instrument, real-time radiography (RTR), was added to the WEAF instrument inventory for examination of physical contents of waste drums. Currently, all CH-TRU and LLW drums generated at ORNL are examined using the RTR unit. In addition, all CH-TRU waste drums are assayed with the PAN and segmented gamma scanning (SGS) systems described below. Only those LLW drums generated at facilities which also generate CH-TRU or remote-handled (RH) TRU waste are currently being assayed. However, in the development of the LLW certification program, plans are being made for all LLW drums to be assayed, primarily due to new requirements imposed in DOE Order 5820.2A.

The route of waste drums through the WEAF begins with an RTR examination, followed by NDA examinations, if required. If a drum is found to contain any items which are prohibited by waste acceptance criteria, called "nonconformance" items, or if the drum itself is found to be defective, the drum is color coded with orange tape and a "REJECT" tag is affixed to it. The drum is then returned to the waste generator for repackaging. A nonconformance report (NCR) is written and accompanies the drum. Copies of the NCR are forwarded to the appropriate quality assurance representatives and a copy is retained at the WEAF. The NCR is also entered into a computerized tracking system where resolution of and corrective actions for the NCR are monitored by the ORNL Quality Department. Table 3 shows a list of nonconformance items which can be detected by RTR examination.

Table 3. Nonconformance Items Detectable by Real-Time Radiography Examination

Free liquids

Compressed gases
    (compressed gas cylinders and aerosol cans),
Lead

Thin-walled primary waste containers

Improperly-positioned lid gaskets

The CH-TRU waste drums are examined to ensure compliance with Waste Acceptance Criteria (WAC) of the Waste Isolation Pilot Plant (WIPP) and ORNL [Reference 3]. After the examination is completed and shows compliance, the CH-TRU waste drums are retrievably stored for eventual shipment to the DOE geological TRU waste repository, the WIPP, located near Carlsbad, New Mexico.

The present routine operation of the WEAF includes NDA and NDE of solid CH-TRU waste and SLLW packaged in drums, certification of these wastes against waste acceptance criteria, issuance of nonconformance reports for drums which fail RTR inspection, and preparation and maintenance of data bases on drums of waste.

REAL-TIME RADIOGRAPHY

The RTR, a TFI Corporation system, uses a 320 kV_{cp} (maximum) variable x-ray tube head. Most waste drum examinations are conducted using an applied voltage of 100 to 150 kV. The duration of an RTR examination of a typical laboratory waste drum containing plastics, cellulosics, and small amounts of metal is approximately one-half hour.

The ORNL RTR radiation control enclosure, or examination chamber, dimensions are 5 ft. x 8 ft. x 8 ft. The examination chamber walls are fabricated of laminated steel, plywood, and elemental lead. The 3/4 in. thick plywood is bonded to the lead sheeting of the side walls and top for structural support and for securing the panels to the chamber frame. The panels of plywood and lead are sandwiched between two sheets of 1/16 in. steel.

The primary shielding for the wall and top of the examination chamber are 1/2 in. thick lead sheets. The side of the chamber to which the x-ray beam is directed is constructed with 3/4 in. thick lead. The additional shielding is required to terminate the x-ray beam and minimize the x-ray penetration to the areas adjacent to the examination chamber.

The chamber door is electrically driven, its motion governed by electrical limit switches at both the open and closed positions. The chamber door contains a 12 inch square leaded glass window and a Bureau of Radiological Health (BRH)-approved safety interlock which interrupts current to the transformers should the door accidentally open.

WEAF NONDESTRUCTIVE ASSAY INSTRUMENTS

Assay Overview

Two NDA instruments are used at the WEAF: PAN assay and SGS. ANSI N15.20 [Reference 4] defines NDA to be:

> "The observation of spontaneous or stimulated nuclear radiations, interpreted to estimate the content of one or more nuclides of interest in the item assayed, without affecting the physical or chemical form of the material.
>
> active assay - Assay based on the observation of radiation(s) induced by irradiation from an external source.
>
> passive assay - Assay based on the observation of naturally occurring or spontaneous nuclear radiation(s)."

The NRC in NRC Regulatory Guide 5.11 [Reference 5] describes the applicable NDA passive measurements:

> "Radiations attributable to alpha particle decay, to gamma-ray transitions following alpha and beta particle decay, and to spontaneous fission have served as the basis for practical passive NDA measurements."

Gamma rays, neutrons, and alpha particles, as well as other subatomic particles, are emitted by various radioisotopes. NDA techniques based on detection of each emitted radiation have been developed and used for CH-TRU and LLW bulk-waste assay.

The passive gamma (SGS) and passive neutron coincidence counting (passive portion of the PAN) methods are techniques which are described by the American Society for Testing of Materials (ASTM), American National Standards Institute (ANSI), NRC, and American Society of Mechanical Engineers (ASME) standards, guidelines, and regulations.

Characteristics of any assay measurement include precision, bias, detection limit. Proper calibration methods must also be employed to ensure unbiased assay results are obtained. Definitions of each of the above terms are given below and were obtained from reference 6.

1. precision: a generic term used to describe the dispersion of a set of measured values.

2. bias: a persistent positive or negative deviation of the method average from the correct value or accepted reference value. (Also referred to as "constant" or "systematic error.")

3. detection limit: a stated limiting value which designates the lowest concentration or mass that can be estimated or determined with confidence and which is specific to the analytical procedure used.

4. calibration: the determination of the values of the significant parameters by comparison with values indicated by a reference instrument or by a set of reference standards.

SEGMENTED GAMMA SCANNING (SGS)

The WEAF SGS unit is a modified Canberra Model 2220-B. The photon detector used is a high-resolution, hyperpure germanium (HPGe) solid state detector.

Originally, the system was capable of quantitatively assaying ^{235}U and ^{239}Pu, exclusively. After completion of recent modifications, the instrument can now acquire data and provide estimates of the quantities of any gamma-emitting isotopes present in amounts above the detection limit. The modifications included expansion of the nuclide search library, using a higher-capacity multi-channel analyzer, rewriting the peak search software, and using a mixed oxide $^{152/154}$Eu transmission source.

Besides fission product isotopes (e.g., ^{60}Co and ^{137}Cs), the number of individual TRU isotopes or their daughters that can be assayed with SGS is relatively large, with ^{233}U, ^{238}Pu, ^{239}Pu, ^{237}Np, ^{241}Am, ^{243}Am among the more common ones. In each case, one or more characteristic moderate-to-high energy gamma rays are emitted in sufficient intensity to permit estimates of quantities in low-to-moderate density waste packages as large as 208 L drums.

To minimize assay errors due to axial inhomogeneities, assays are performed in segments along a waste package's vertical axis. Radial inhomogeneities are minimized by rotating the drum during the assay measurement. The detector is shielded in such a manner so as to allow the waste drum to be scanned in segments. Typically 10 to 20 segments are used.

Gamma-ray attenuation is measured for each segment with a transmission source usually located on the detector casing. The energy of this source is selected to match that of the gamma-ray energies being measured. ORNL uses a mixed ^{152}Eu/^{154}Eu oxide source for its large array of gamma-emitting radioisotopes (50 keV to 1600 keV), while ^{75}Se is typically used for ^{239}Pu assays.

Counting electronics allow dynamic counting rate ranges of factors of 10^4 to 10^5 or more. Dead-time corrections are measured with a second small, low-energy source positioned near the detector. Waste packages are automatically rotated about their vertical axes and cycled through the required segment heights with standardized, computer-controlled electronic motors and precision mechanical turntable and elevator hardware.

Some of the factors affecting assay measurements are particle self-absorption and nonhomogeneity of the assayed item ("lumping"). Two conditions must be met to optimize assay results: (1) the particles containing the radionuclide must be small to minimize self-absorption of emitted gamma radiation, and (2) the mixture of material within a package segment must be reasonably uniform in order to apply an attenuation correction factor. The attenuation correction factor is computed from a single measurement of gamma ray transmission through the segment. Variations in waste composition and density within a vertical segment lead to indeterminate errors. Such variations should be minimized through strict scrap and waste segregation procedures.

A combination of analytical error analysis [Reference 11] and experimental usage over many years has determined that transmission factors greater than or equal to 0.5 percent are required for accurate SGS assays, although some researchers have reported lower transmission factors. Subject to that limitation, any chemical or physical waste form may be assayed using the SGS method. The physical density of a waste package, under the limitation of transmission factor size, depends greatly on the package size (i.e., the radial distance from the gamma- emitting source(s) to detector). Four-liter packages having densities as high as 2 g/cm^3 meet the criterion, whereas 208 L packages are limited to densities of 0.5 g/cm^3 or less. To assure compliance with these limits, the SGS software package includes an automatic warning, recorded on paper and magnetic media for archival purposes, indicating when the transmission factor for any sector falls below the prescribed limiting value. The routine practice is to calculate a contribution from that sector based on the lower-limit transmission (e.g., 0.5 percent).

The reason for maintaining the assay value, rather than disregarding it, is that most SGS transmission failures occur for only one sector out of the 10 to 20 drum sectors assayed. This sector, on the average, contains only a small fraction of the waste drum's total TRU inventory of gamma-emitting isotopes. Estimating the TRU content for one, two, or three such failed segments in this fashion results in only a small overall assay error for the waste drum. Since the SGS assay value for a transmission failure is truly a lower limit, and passive neutron assays generally provide upper limit assay values, especially for TRU isotopes, the combination of SGS and passive neutron assay methods tends to bracket the true concentration of radionuclides in the waste.

Some waste matrices are inherently unsuitable for SGS analysis. Such forms may contain 'lumps' of radionuclides, that is, radionuclides contained in small volumes of waste having a localized density substantially different from the bulk density of the rest of the container. The particle dimensions that constitute a lump vary with the energy of the radiation being measured. For example, a plutonium metal sphere 0.02 cm in diameter will absorb approximately 4% of the 414 keV, ^{239}Pu gamma rays produced. Approximately 15% of the 186 keV gamma rays of ^{235}U will be absorbed in a uranium metal sphere of the same diameter.

As mentioned previously, another condition that will cause measurement problems occurs in containers with several irregular regions, highly variable in density, that prevent the calculation of a valid attenuation correction based on the transmission measurement. In case of such a condition, an analytical method less sensitive to nuclide and matrix densities, such as passive neutron coincidence counting (PNCC), should be employed.

Careful inspection of the transmission and nuclide peak areas for each segment may provide clues when a measurement should be suspect. Sudden, discontinuous changes in the transmission values for adjacent segments or high counts for isolated segments are examples of signals indicating possible problem items.

SGS Assay Precision and Bias

Repeatability of results in typical SGS systems, when operated and calibrated according to the recommended procedures, is limited only by radioactive decay statistics and related counting errors. Counting statistics, in turn, are a strong function of TRU isotopic loading and counting time.

Reference 7 discusses SGS precision and bias in detail. The precision of a SGS assay is a function of the precision of the measured peak areas for each segment. The precision of an assay is normally better when the following conditions can be obtained:

- Long count time
- High transmission source activity
- Low gamma attenuation at the energy being measured

The precision of an assay is not strongly related to the presence of an ideal matrix and nuclide density. However, measurement bias depends primarily on small particle size and homogeneity. Negative bias will be encountered when the nuclide is present in lumps that attenuate their own radiation to a greater extent than the surrounding material. Positive bias can result from low transmission items with over-corrected end effects. Items containing high-density areas may be biased either high or low or be unbiased, depending on the relative position of the high density area and the nuclide of interest. In the majority of measurement situations, however, it is expected that when biases exist, measurement results will be lower than true values.

SGS and destructive assay comparison studies of several waste forms indicate SGS assay biases of 10 percent or better at the 95 percent confidence level [Reference 12]. Assay biases for low-density waste matrices contained in 208 L drum packages are 5 percent or better. In small packages, SGS assay biases of better than 0.5 percent have been reported [Reference 5]. The basic assay formalism associated with the SGS method, that is, transmission correction and the use of small segments, is conducive to very accurate results if recommended procedures are correctly followed. Heterogeneous matrices and isotopic concentration can have a severe effect on assay bias.

WEAF PASSIVE-ACTIVE NEUTRON ASSAY SYSTEM

PAN assay systems consist of two independent neutron assay units: passive and active. The combination of passive and active neutron assays within a common system provides a unique set of information.

The passive assay method described below is an adaptation of the PNCC method using "self-measurement" matrix corrections. Two complete passive assay detection systems are maintained with separate counting electronics. The passive coincidence measurement provides quantitative information on isotopes with even mass numbers, such as ^{240}Pu, which are present in the waste container. The passive singles neutron count rate, which is the difference between total neutron rate and that due to spontaneous fission events, provides semi-quantitative information on alpha particle emitters present in the waste container, such as ^{241}Am. The active assay provides quantitative information on the ^{239}Pu and other fissile isotope constituents of the waste.

For example, for weapons-grade plutonium, the passive coincidence and active assays provide independent total Pu assay values. This fact has been extremely important in verifying the accuracy or determining the bias of the PAN assay measurement technique. [Reference 8]

PAN Instrumentation:

A cross-sectional view of the ORNL PAN detection system, showing the schematic "interwoven" layout of the two distinct types of neutron detection packages, bare ^{3}He and cadmium (Cd)-shielded ^{3}He detector tubes, is shown in Figure 1.

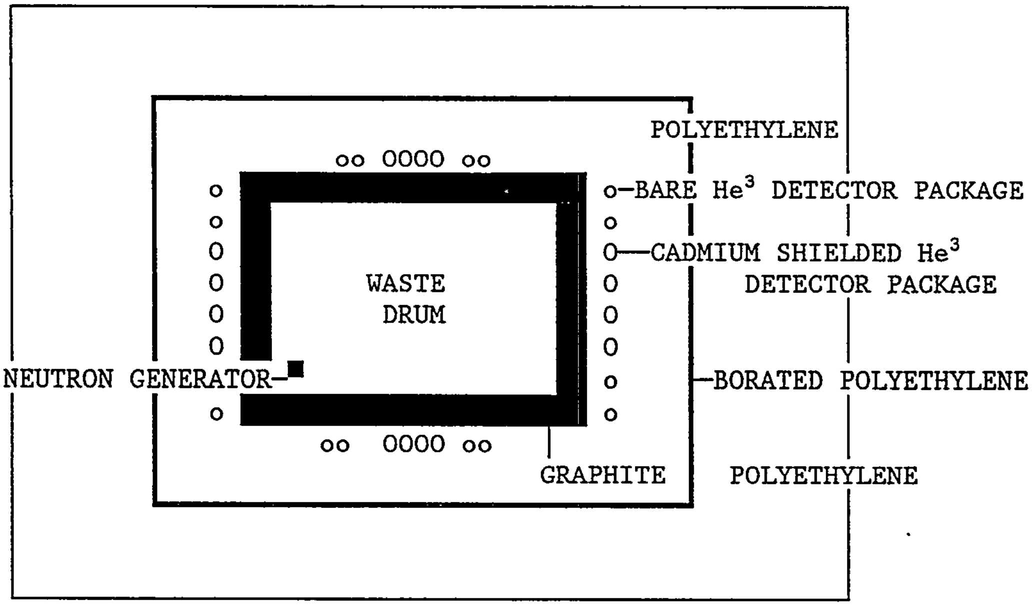

Figure 1. Cross Section View of Passive/Active Neutron Assay System

Passive Assay Portion

The passive portion of the PAN assay system uses the two types of detectors to determine a moderator index (MI) used to make systematic matrix corrections, and optimize counting statistics depending on the actual relative neutron sources encountered.

For low count-rate waste containers all counts detected by the neutron detectors are summed to yield the lowest assay limit of detection possible. All detector count rates, acquired by both bare and shielded detectors, are summed electronically to obtain a "System Totals" neutron detection efficiency of approximately 12 percent.

For waste containers with higher TRU isotopic loadings (e.g., 100 g or more) coupled with strong (alpha, n) backgrounds, the cadmium-shielded detectors are summed independently, and the "Shielded Totals" count rate is formed with a resulting neutron detection efficiency of 2.9 percent. However, this detection package possesses a much faster "die-away" or "neutron-collection" time, approximately 15 microseconds, about six times faster than that of the slower "Systems Totals". At low count rates the slower collection time is of no consequence, since accidental coincidences due to (alpha, n) reactions are small. Therefore, the Systems Totals provides not only a more sensitive but also statistically more precise passive assay measurement.

At higher data collection rates this is no longer true. The faster die-away time of the Shielded Totals becomes more important statistically than the neutron detection efficiency. As a consequence, at high neutron count rates the Shielded Totals Coincidence rate is used to obtain the more precise passive assay measurement value.

The cross-over count rate (i.e., the count rate at which the assay measurement value obtained by the Shielded Totals supplants the Systems Totals) has been experimentally determined to be approximately 2000 counts per second (cps Systems Total count rate). This value is used in the assay algorithm. There is a substantial range in which either Systems Coincidence or Shielded Coincidence rates both provide precise assay values.

Active Assay Portion

The active portion of PAN systems performs a high-sensitivity, pulsed thermal neutron interrogation assay of waste drums. As shown schematically in Figure 1 a small 14-Mev neutron generator has been placed within the assay chamber between the waste drum and moderating walls to provide short pulses (5-10 microseconds) of high-energy interrogating neutrons. In approximately 0.5 ms all original fast neutrons in this interrogating pulse have been thermalized by multiple collisions with the graphite and polyethylene walls and with moderating materials within the waste drum. This "thermalized interrogating pulse" persists with a half-life of about 400 us, during which time induced fissions within the waste drum are produced, primarily in ^{239}Pu or other fissile isotopes. These events, in turn, result in a burst of prompt-fission spectrum neutrons emitted by each fissioning nucleus.

The cadmium-shielded detection packages have been designed to reject an external thermal neutron flux to 1 part in 10^7, but to respond sensitively to fission spectrum neutrons. The summed shielded detector packages shown in Figure 1 detect about 10 percent of all induced fission events produced within typical waste drums.

An additional measurement feature not shown in Figure 1, but discussed at length in reference 8, is the set of thermal flux monitors, one cadmium-shielded and collimated and the other bare, that are also positioned inside the assay chamber between the waste drum and the moderating walls. As discussed at length in reference 8, the ratio of these flux monitors is highly sensitive to the total neutron absorption characteristics of the waste drum contents. This ratio is used to form a drum "Absorption Index" (AI).

PAN Assay Matrix Corrections

Two types of matrix effects can interfere with the active neutron measurements: absorption and moderation [Reference 8]. The absorption effects occur almost entirely as an attenuation of the interrogating thermal neutrons, caused by the presence of various neutron poisons (e.g., boron, cadmium, etc.) within the waste matrix.

Moderation effects occur at two stages of the measurement. The original burst of 14-Mev neutrons can be moderated to a considerable extent during passage through the waste matrix. Generally, this results in a larger thermal neutron interrogation flux than would have been produced in the absence of matrix. After the interrogation flux has produced fission reactions within the waste matrix, the same moderating materials can attenuate the prompt-fission signal neutrons, resulting in a decrease in observed response relative to the no-matrix case. This attenuation of fission-neutrons is also the primary matrix effect for the passive measurement.

The approach to matrix corrections has been to base corrections on measured quantities determined as adjuncts to the primary active and passive TRU assay measurements. The systematic matrix correction algorithm is based on an analytic fit to assay measurements obtained for different positions of the source within a matrix drum. These analytic fits then provide estimates of uncertainty for the active and passive assay data.

The absorption matrix correction approach used by the PAN systems employs a ratio of an unshielded in-chamber flux monitor to a cadmium-collimated, in-chamber flux monitor (designated the barrel flux monitor). This ratio is called the AI. The barrel flux monitor detects those neutrons which have undergone drum matrix interactions. The ratio of the monitors strongly reflects the neutronic properties of the matrix.

Absorption Index
= [flux monitor response (0.7-4.7ms)]/[barrel flux monitor response (0.7-4.7ms)] (1)

The moderator index depends upon the responses of the two detection systems (cadmium-shielded and bare) to moderated neutrons. The shielded detectors are insensitive to thermal neutrons, while the bare detectors are very sensitive to the thermal neutron flux. In turn, the thermalized fraction depends very strongly on the moderator density of the matrix. To use this relationship in obtaining matrix correction factors, the ratio is normalized so that a value of zero is obtained when no moderator is present and a small correction is made to account for self-absorption effects.

$$\text{Moderator Index (MI)} = \{1 - [(\text{shielded totals})/(\text{system totals})]/A_o\} \times \{A_1 + A_2 \times \ln(\text{absorption index})\} \quad (2)$$

The term within the first set of brackets is the basic raw spectral data. The term within the second set of brackets is the correction term for matrix absorption effects. The same MI values are used for both active and passive matrix corrections.

In order to obtain data to construct the analytical models of matrix correction factors, nineteen simulated waste matrices were fabricated [Reference 8] and active and passive calibration standards were placed in known locations throughout the waste matrix drums. Both active and passive assay matrix response measurements were obtained as a function of position (radius, r, and height, z) of the standards. The resulting matrix response values varied smoothly as a function of r and z. These studies determined that the systematic effects are due only to gross neutron absorber and moderator amounts and are independent of the actual nature of the materials themselves. That is, a drum filled with Rashig rings (borated glass) produces the same responses as a drum filled with vermiculite mixed with an equally absorbing amount of borax.

Most of the observed distributions have been found to fit a power law as given in equation 3:

$$y = A + Br^N \quad (3)$$

where A, B, and N are the curve fit parameters and r is the drum radius.

Volume-weighted average values were calculated using this equation, representing the most probable measurement result for either a totally uniform or a totally random distribution of source material within the matrix.

The matrix correction factor (MCFA) for an active assay measurement is a function of the AI and MI.

$$\text{MCFA} = \text{MCFA(AI)} \times \text{MCFA(MI)} \quad (4)$$

The MCFA values were fit to the power law (equation 3) as a function of their AI values for the 19 simulated waste matrices. The following set of equations describing the absorption portion of the active assay matrix correction factor were obtained:

$$\mathrm{MCFA(AI)} = 1.00 \tag{5}$$

for the AI less than or equal to 2.72, and

$$\mathrm{MCFA(AI)} = 0.54\mathrm{x}(\mathrm{AI})^{0.612} \tag{6}$$

for the AI greater than 2.72.

The moderator portion, MCFA(MI), of the active assay matrix correction factor is obtained by dividing the total measured MCFA values by the calculated MCFA(AI) values obtained in equations (5) or (6).

The analytic representation of these data is thus of the form

$$\mathrm{MCFA(MI)} = 1.00, \tag{7}$$

for the MI less than or equal to 0.40,

$$\mathrm{MCFA(MI)} = 0.483\exp[1.817(\mathrm{MI})] \tag{8}$$

for the MI greater than 0.40.

The passive neutron matrix corrections are determined by systematic drum matrix measurements in a manner similar to the active measurements discussed previously. The passive matrix correction factors, MCFP, are a function of only the MI.

The MCFP analytic fits to the four independent quantities measured during a passive assay scan are given below.

$$\mathrm{MCFP(system\ totals)} = 1.00, \tag{9}$$

for the MI less than or equal to 0.355,

$$\mathrm{MCFP(system\ totals)} = -0.16 + 3.28(\mathrm{MI}), \tag{10}$$

for the MI greater than 0.355,

$$\mathrm{MCFP(shielded\ totals)} = 1/[1 - \mathrm{MI}], \tag{11}$$

$$\mathrm{MCFP(system\ coincidence)} = [(0.5967)/(1 - \mathrm{MI}) + 0.4187]^2, \tag{12}$$

$$\mathrm{MCFP(shielded\ coincidence)} = [(0.8902)/(1 - \mathrm{MI}) + 0.2337]^2. \tag{13}$$

The matrix correction equations given above are contained in the present PAN assay systems algorithms used throughout the DOE. The MI varies smoothly with average hydrogen density within a 208 L drum. Sludges display one of the highest average hydrogen densities, with correspondingly high MI's (0.4 to 0.8) of any CH-TRU waste form. Lightly moderating matrices, such as combustibles, have MI's falling typically in the 0.1 to 0.3 region, and miscellaneous metals matrices, which generally contain no moderating materials, have measured MI's near 0.0.

The MCF value is the multiplicative factor required to normalize a given matrix measurement to the empty drum level of PNCC sensitivity. The MCF value varies smoothly as a function of the MI; A graph of MCF versus MI can be used to estimate typical MCF values. For example,

(a) Miscellaneous metals, MCF = 1.0 (i.e., same sensitivity as with empty drum),

(b) Combustibles matrix, MCF = 1.35, and

(c) Sludges, MCF = 3.6.

PAN Assay Algorithm and Data Acquisition System

The ORNL PAN unit is equipped with an IBM/PC-based data acquisition systems as described in reference 13. The system operating program (NEUT) controls all data acquisition and contains the assay algorithm.

To begin data acquisition, the operator enters drum identification, content code information, drum weight, and similar data from the PC keyboard, from a bar code reader, or from direct interaction with the site data management computer. This is followed by sequential active and passive neutron assays. The weight of the drum's contents is used in calculating the specific activity (nCi/g) of TRU isotopes which differentiates between TRU and non-TRU wastes. The content code is used to flag difficult-to-assay matrices or "special case" drums.

Measured data, initialization information, date and time stamp from the internal PC clock, and final analysis results are archived on both floppy and internal hard magnetic disks. An on-line hard copy printout of the assay parameters and results is generated. All background and calibration measurements are routinely recorded and archived in the same fashion as normal assays. Thus, a continuous and traceable record of all data is maintained.

The PAN assay systems are comparatively recent developments in NDA instrumentation, having come into practical use in the last six years. Consequently, ASTM and ANSI standards have not yet been developed for these assay systems. Active assay techniques have been used for approximately 18 years, but 14-Mev thermalized neutron assay, which constitutes the active portion of PAN, is comparatively recent. The passive coincidence portion of PAN is similar to the PNCC assay technique. Therefore, ASTM, ANSI, and NRC standard practices and guidelines for PNCC are followed for that portion of the PAN system.

The assay procedure for PAN units equipped with the IBM/PC data acquisition system is relatively straightforward. An operator inserts a waste drum into the PAN unit and enters all drum identification information through an interactive dialogue with the PAN assay system software, NEUT. Once NEUT has checked the information for correct format, the assay record and programmable electronics hardware are properly indexed and prepared. NEUT then displays a message that the system is ready to begin assay.

At this point, the operator presses the start button on the MA165C neutron generator controller unit to initiate PAN active assay. At the conclusion of the active assay, NEUT automatically records all data and initiates the PAN passive assay. At the conclusion of the PAN passive assay, all data is recorded, analyzed and printed out for immediate inspection. The system is then ready to perform another assay.

PAN Assay Precision, Bias, and Limit of Detection

The PAN assay algorithm contains a calculation of measurement error [Reference 8] that combines statistical and estimated systematic errors based on the measured matrix correction factor. For a generally heterogenous matrix and TRU materials distribution, the larger the indicated matrix correction, the larger the expected assay error. These values are reported with the actual assay values, for both passive and active neutron assays. For many waste streams a typical value for the estimated systematic error (not including the statistical contribution to the error) is 20 percent. When a systematic matrix correction formalism is used, the corresponding error in the passive assay measurement can be decreased to 5 percent or less for dry, combustible, low-hydrogen content waste, such as general laboratory waste.

The passive assay precision is calculated as for PNCC, with the addition of a term representing the uncertainty in the matrix correction factor. The algorithm used in the passive coincidence portion of the PAN calculates a composite assay error based on combining all the effects discussed above, which becomes part of the permanent archived assay record.

The active assay precision estimate includes a systematic error contribution, which is a function of the matrix correction factor (AI and MI). For reasonably homogeneous matrices, AI measurements indicate one sigma relative errors of ± 10 percent. For nonhomogeneous matrices, the variance is a function of the magnitude of the matrix correction factor [Reference 8]. That is, the larger the matrix correction factor the larger the associated variance of the assay. Distributional errors have been calculated and plotted as a function of the total matrix correction factor. For example, a matrix correction factor of approximately five yields a corresponding relative error (one sigma) of 50% in the assay measurement. Table 4 summarizes PAN assay biases.

Table 4. PAN Assay Bias

Matrix Correction Factor,MCF	Percentage Error
1.0*	20
4.0	30
5.0	50

* MCF = 1.0 corresponds to a "no matrix correction" case.

Extensive comparisons have been performed for passive and active neutron assays of the same drum and a variety of matrix types, such as sludges, job-control wastes, combustibles, graphite scarfings, miscellaneous metals, tantalum crucibles, glassware, molten salts, filter media, dirt, and others. The matrix corrections applied to passive and active assays for a given type of matrix (except where no matrix corrections are necessary) are quite distinct. Thus, the probability of obtaining agreement between active and passive neutron assays for wastes with significant moderator and absorber amounts by accident or coincident matrix correction factors, is virtually negligible. That is, if one obtains agreement, both independent PAN assay techniques are considered to yield unbiased assay measurement values.

The assay limit of detection for the active neutron portion of the PAN unit is approximately 1 mg ^{239}Pu placed anywhere within a typical 208 L waste drum.

Decision-Tree Analysis

Two independent assay values, a "passive" mass and an "active" mass, are obtained with each PAN assay. A "decision-tree analysis" is performed within the assay algorithm to determine the most representative value. The default decision is to choose the active assay for low Pu mass (< 10g) and the passive assay for high (≥ 10 g) high Pu mass.

When specific content code or matrix information is available that indicates, for example, that passive assay results are more reliable than active assay results for that content code, then the algorithm selects the passive assay results. Similar overrides involve the statistical accuracy of a measurement. For example, if the passive measurement has a large error associated with it, then the active measurement is selected.

CONCLUSION

Waste characterization is the most important part of certifying that wastes meet a given set of waste acceptance criteria. A variety of methods and techniques may be used to characterize wastes, including material accountability, process knowledge, and direct or indirect measurements. In this paper, several techniques for direct measurement of radionuclide content, physical form, and chemical composition were discussed, including measurements which can be made at the generator level before waste is packaged into transportation containers, measurements that made be made on bulk waste containers after packaging, and verification of certain measurements by sample collection and analysis. Several waste characterization approaches are being employed at the Oak Ridge National Laboratory.

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WASTE REDUCTION AND MINIMIZATION

WASTE MINIMIZATION POLICIES, REGULATIONS, AND PRACTICES
within the
U.S. DEPARTMENT OF ENERGY DEFENSE PROGRAMS

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ABSTRACT

In 1984 the U.S. Congress enacted the Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA). One of the goals of this legislation was to focus attention on the need reduce or eliminate hazardous waste so as to minimize the threat to human health and the environment. Subsequently, in September of 1988, DOE issued a Radioactive Waste Management Policy, DOE Order 5820.2A, and in November a General Environmental Program Order, DOE Order 5400.1. These documents embrace the principles set forth in RCRA, and expand their scope to include radioactive, mixed, and pollutant waste, and all actions for reducing waste from the point of generation through waste treatment, storage, transportation and disposal.

This paper will present an overview of the legislation and policies for waste reduction and, in addition, give site responsibilities for implementing waste reduction program activities.

INTRODUCTION

The United States is going through a cultural change due to potential adverse impacts of hazardous materials on human health and the environment. The cultural change includes elimination/reduction in the generation of hazardous waste. As the U.S. became the world leader in technology, potential impacts, nationally and world-wide realization of various types of contaminants emitted to the environment became a major concern. Cost of waste treatment and emission controls rose exponentially over the years; however, these escalating costs have had severe impact on the economy of this nation. One of the solutions is the prevention of hazardous waste at the source substituting non-hazardous materials for hazardous materials. Applicable Federal laws and regulations discussed in this paper, reflect actions taken to safeguard human health and to protect the environment.

WASTE MINIMIZATION POLICIES, REGULATIONS, AND PRACTICES
within the
U.S. DEPARTMENT OF ENERGY DEFENSE PROGRAMS

FEDERAL REGULATIONS

In 1965 the Solid Waste Disposal Act was passed with the primary purpose of improving solid waste disposal methods. The Act was then amended in 1970 by the Resource Recovery Act, and once again in 1976 by the Resource Conservation and Recovery Act (RCRA).

The purpose of RCRA is to ensure the safe and environmentally acceptable management of solid wastes. Specific goals of this legislature are:

- enhancing protection to human health and the environment;
- reducing waste and conserving energy and natural resources; and
- reducing or eliminating the generation of hazardous waste as expeditiously as possible.

The Act was then amended in 1980 and again in 1984. The second amendment is the "The Hazardous and Solid Waste Amendments (HSWA) of 1984." The Congressional mandate for waste minimization within HSWA is:

> "...it is to be a national policy of the United States that, wherever feasible, the generation of hazardous waste is to be reduced or eliminated as expeditiously as possible. Waste that is nevertheless generated should be treated, stored, or disposed of so as to minimize present and future threat to human health and the environment."

On September 1, 1985, several requirements for waste minimization became effective under the HSWA. These requirements were codified by the EPA in its Code of Federal Regulation (CFR) 40, Parts 262, 264, and 265. These requirements affect the generation of waste as well as its transportation and treatment:

- Generators of hazardous waste who ship waste off-site, and generators who also treat, store or dispose of hazardous waste on-site at permitted and interim facilities, are required to submit biennial reports which describe:
    - efforts undertaken during a given year to reduce the volume and toxicity of waste generated; and
    - changes in volume and toxicity of waste actually achieved during the year in question, in comparison with previous years, to the extent such information is available [HSWA Section 3002 (a-d), 40 CFR Parts 262.41 (a) (6) and (7); 264.75 (h) and (i); and 265.75 (h) and (i)].

- Owners or operators of hazardous waste treatment, storage, or disposal facilities, where such waste was generated, must certify annually, as a condition of their permit, and as part of their operating record if they are also the generators of hazardous waste, must certify in their shipping manifest, that
  - the generator of the hazardous waste has a program in place to reduce the volume or quantity and toxicity of such waste to the degree determined by the generator to be economically practical; and
  - the proposed method of treatment, storage or disposal is that practicable method currently available to the generator which minimizes the present and future threat to human health and the environment [HSWA Section 3005 (h)(1) and (2); Section 3002 (b)(1) and (2); and 40 CFR Part 264.73 (b)(9)].

Title III of the Superfund Amendments and Reauthorization Act (SARA), the Chemical Emergency Preparedness and Community Right-to-Know Program, also has an optional waste minimization reporting requirement. The Agency regards this reporting as an opportunity for a facility to notify the public of its efforts.

DOE REQUIREMENTS

In addition to the Amendments, the DOE has issued policies and directives for a waste minimization program plan, as well as specific procedures for minimizing radioactive, hazardous, and mixed wastes

In DOE Order 5400.1, Chapter III, 4. (b) the "General Environmental Protection Program" requires preparation of a program plan of considerable scope and detail:

> ". . . a Waste Minimization Program (plan) that will contain goals for minimizing the volume and toxicity of all wastes that are generated, with annual reductions if programmatic requirements allow. Changes in waste quantity, volume, and toxicity that are achieved shall be compared with quantities generated in the previous year. The proposed methods of treatment, storage, and disposal that accomplishes waste minimization that are technically and economically practical shall be reported as appropriate. Waste minimization plans required by specific legislation, such as RCRA, shall be included as part of this program plan."

The site plans are to completed by May 1990, and, thereafter, the plan is to be reviewed annually and updated every three years.

Draft DOE Order 5400.ZZ, the Hazardous and Radioactive Mixed Waste Program, also states that its DOE's policy to implement waste minimization measures, as specified in RCRA, for hazardous, radioactive, and mixed wastes.

In DOE Order 5820.2A, "Radioactive Waste Management," the policy specifies compliance with applicable regulations, stating:

> "The generation, treatment, storage, transportation, and/or disposal of radioactive waste, and other pollutants or hazardous substances they contain, shall be accomplished in a manner that minimizes the generation of such wastes across program office functions and complies with all applicable Federal, State, and local environmental, safety, and health laws and regulations and DOE requirements."

In DOE Order 5820.2A, Radioactive Waste Management, specific activities are detailed for waste reduction for each of the waste categories: High-Level, TRU, and Low-Level. Following are directives for each category, as applicable:

- High-Level Waste [Chapter I, (7) (a)]

  "For the purpose of economy and enhancing the safety of high-level waste storage, processing programs shall be developed and implemented at the generating site to reduce the quantity of waste being sent to storage, and techniques (e.g., evaporation) shall be implemented to reduce further the waste volume in storage."

- TRU Waste [Chapter II, 3. (b)]

  "Technical and administrative controls shall be directed to reducing the gross volume of waste generated and/or the amount of radioactivity requiring disposal. Transuranic waste reduction efforts shall be based on the implementation of techniques such as process modification, process optimization, materials substitution, decontamination, assay of suspect waste, and new technology development. Volume reduction techniques, such as incineration, compaction, extraction, and shredding shall be implemented wherever, cost effective and practical."

- Low-Level Waste [Chapter III, 3. (c) and (f)]

  "Technical and administrative controls shall be directed to reducing the gross volume of waste generated and/or the amount of radioactivity requiring disposal. Waste reduction efforts shall include consideration of process modification, process optimization, materials substitution and decontamination."

  "All DOE low-level waste generators shall establish programs (goals, incentives, procedures , and reports) to assure that the amount of low-level waste generated and/or shipped for disposal is minimized."

  "Each DOE low-level waste generator shall separate uncontaminated waste from low-level waste to facilitate cost effective treatment and disposal."

> "Each DOE low-level waste generator preparing a design for a new process or process change shall incorporate principles into the design that will minimize the generation of low-level waste.
>
> "Waste treatment techniques such as incineration, shredding, and compaction to reduce volume and provide more stable waste forms shall be implemented as necessary to meet performance requirements."

Once a year, each site is to prepare a summary of waste reduction activities as an appendix to the site's Waste Management Plan. The report has three principal points. First, the report is to describe how the waste minimization program is structured; secondly, what waste minimization techniques are being used and the merits of each; and thirdly the performance of the waste reduction program, i.e volumes of waste and radionuclides reduced from the previous year as a result of waste reduction activities.

DEFINITIONS

The definitions and use of the terms "waste minimization, waste reduction, waste avoidance, and pollution prevention" have caused a tremendous amount of misunderstanding and confusion within the waste management community.

The DOE Defense Programs defines "waste minimization" as any action that minimizes the volume or toxicity of waste by avoiding its generation or by recycling or reuse. The term "waste reduction" is waste minimization plus any waste treatment that reduces the volume or toxicity of waste requiring disposal.

The EPA in a Federal Register Notice of January 26,1989, under Section II, "EPA's Pollution Prevention Policy", states that the term, "waste minimization," which EPA has previously used in reference to source reduction and recycling activities in its hazardous waste program, has been replaced by the phrase "pollution prevention." The EPA, therefore, has focused on preventing waste at the source as the first choice, and recycle and reuse as a second choice; both, of which, have preference above treatment, control, and disposal.

IMPLEMENTATION OF FEDERAL AND DOE REQUIREMENTS

Consequently, reporting and reference to waste minimization/reduction should encompass all wastes: liquid, solid, and airborne within the categories of high-Level, TRU, low-level, hazardous, and mixed.

Activities for waste minimization/reduction may include any action from generation to disposal, such as process design or improvement, substitution of materials, waste segregation and recycling, waste treatment and processing, and administrative controls, such as through procurement, and training for waste awareness. In addition, consideration should be given to remedial actions and decontamination and disposal activities.

Further, we believe, at this time, all "waste minimization" reporting requirements by EPA should be under the term "pollution prevention."

The policy, therefore, is to first, avoid as far as practicable the generation of low-level, high-level, transuranic, hazardous, and mixed waste and to reduce the toxicity of waste streams containing hazardous components. Secondly, where wastes are unavoidably generated, attempts should be made to recycle or reuse all or part of the waste stream components, and, finally treat non-reusable waste to further reduce the volume or toxicity.

Consequently, from a programmatic perspective in implementing this system, the DOE is assuring, that each waste generating site has:

1. An organized, comprehensive waste minimization program that reflects the goals and policies set by Congress, the EPA, the DOE, the state, and other affected regulatory agencies.
2. A Waste Reduction Coordinator or Manager, who is supported by upper management.
3. A waste minimization plan with specific actions such as training and waste reduction awareness, waste stream characterization, methods and technologies to further waste reduction, and a reporting system that will include monitoring, auditing, and providing value engineering on existing processes.

Strategic elements for a waste minimization/reduction plan should include the following topics:

Purpose:

The stated purpose of the site waste minimization/reduction plan is to provide an overall structure to a waste minimization/reduction program. The objectives for each plan, as amended for specific sites, should be stated clearly and succinctly. The purpose statement should include the concepts introduced above, as set forth in DOE Orders, in a statement of basic philosophy for minimizing waste, i.e reduction in radiation exposure, protection to the environment, and cost/benefit factors.

Introduction/Background:

The introduction to each plan should provide a brief description of the site itself, which entails a discussion of the mission of the particular site, its overall program for waste minimization and treatment, as well as an overview of its objectives and scope of operation.

Program and Organization:

A waste minimization program is an organized, comprehensive, and continual effort to accomplish waste reduction. Successful waste minimization programs begin with top management commitments to reduce waste. Top management support at DOE facilities may be demonstrated by a written policy assuring upper management support for waste minimization and a commitment to implement recommendations identified through assessment, evaluation, or other means.

The program should have a Waste Reduction Manager, who provides guidance, coordination, and accountability for waste minimization at the site, and a DOE Site Waste Reduction Program Monitor who has oversight responsibility to assure waste minimization activities are taking place according to the regulatory requirements and DOE Orders.

The descriptive text should include the appropriate organizational charts and directives which delineate, authority, responsibility, accountability, and lines of communication and reporting system.

Waste Stream and Production Process Assessment:

Waste types, volumes, hazardous chemicals, radionuclides, and levels of toxicity should be identified within the plan and tracked by a systems approach. This action should establish baseline levels and provide an insight to targets of opportunity for waste minimization/reduction.

A source from which further provisions for the performance of waste minimization assessments can be derived is the EPA document entitled Waste Minimization Opportunity Assessment Manual, EPA/625/7/88/003, July 1988. The performance assessments may, or may not, apply to a site operation, but the generic approach could be consideration for application.

Methods and Technology:

Methods and technology for waste minimization/reduction may include any action from generation to disposal, such as source reduction through procurement control and administrative usage, process design or improvement, substitution of materials, waste segregation and recycling, and waste treatment.

Procurement control and administrative usage of hazardous materials can be applied to restrict the volumes of hazardous waste produced. To augment the control, a computerized tracking system can be implemented for tracking all hazardous materials such as chemicals, acids, solvents, degreasers, lubricants, and paints. For procurement control, hazardous items ordered need approval by an authority who reviews the request. The reviewing authority determines if alternative non-hazardous materials might be applicable, volumes requested are reasonable, and if the material might be available from an on-site source with excess stock.

Improvements in process design or operation can significantly impact waste volumes and toxicity levels. For example, the improvement may be improved process efficiency and thus reduce the consumption of feed materials.

Examples of substitution of materials, as applied to waste minimization, can be 1) the avoidance of hazardous constituents within a waste stream such as substituting a non-hazardous solvent for a hazardous one, or 2) increase the life expectancy of equipment or facilities such as using tantalum for stainless steel in corrosive environments.

Waste segregation is normally applied to separate wastes in order to maximize treatment and disposal efficiency, assure hazardous wastes are not mixed with non-hazardous wastes, reclassify wastes, and to identify items that may be recyclable. An example may be the implementation of an assay system so that suspect-radioactively contaminated waste can be sorted into radioactively contaminated and non-radioactively contaminated categories.

Recycling activities include the use, reuse, reclamation and resource recovery techniques to return a potential waste material to either the originating process as a substitute for a feed material, or to another process as an input material. Recycling may also include the use of on-site facilities as appropriate. Reclamation is the recovery of a material from a potential waste.

As a final step, non-usable waste can be treated to further reduce the toxicity and/or volume. These treatments may include, but are not limited to, melting, evaporation, incineration, compaction, and chemical conversion of the hazardous components to non-hazardous.

Quality Assurance:

Quality assurance program objectives and methods should be identified and if applicable implemented into the waste minimization/reduction plan. DOE Order 5700.6 (b) specifies the need for a Non-Weapons Quality Assurance (QA-1) Program, and objectives of the Order are to give some assurance to the quality of site programs such as waste minimization/reduction. For example, how are procurement systems implemented to assure quality items are being purchased which will last longer in harsh environments. Another example, may be to assure during the design and development of processes and equipment that considerations are being given to the quality factors for waste reducing waste.

Technology Transfer:

Technology transfer on concepts or methods for waste minimization/reduction within an organization is important where similar, multiple facilities or processes exist. For example, newsletters and presentations could be used to transmit information for minimizing waste within the design or modification of a facility, reuse or recycling of solvents and coolants, or new or novel techniques for waste treatment.

Such waste minimization efforts and techniques also can be effectively shared with other DOE facilities and other federal agencies, as well as with private industry and the international community.

Goals, Schedules, and Tracking Systems:

Goals and schedules for waste minimization/reduction should be prepared for the plan and updated periodically. The goals and schedules should focus on implementation of methods and technologies for waste reduction which could also include implementation of policies, procedures, training, assessments, and evaluations. A comprehensive tracking and reporting system needs to be included with the goals and schedules which will reflect status and benefits being derived from the waste minimization/reduction program.

As a site option, percentages or volumes or toxicity levels for quantities of waste reduced can be included. These values can be established on waste volume per production unit, or some other relevant measure of waste minimization. Noted, however, waste volumes or toxicity levels as a function of time or historical data can be misleading if production operations fluctuate with schedules.

Training and Incentives:

Waste minimization/reduction training should be instituted for all employees. Employee job assignments and waste produced from that job should be evaluated periodically to determine if waste training and awareness is impacting waste volumes or toxicity values.

Waste minimization awareness at the site can be promulgated through presentations and briefings, publications, and newsline items placed on bulletin boards.

Incentives for minimizing waste can be established through monetary or recognition means such as impacts to the contractors Cost Plus Award Fee (CPAF) and awards and citations to an organization or employee. Other incentives, however, may be in the form of a reduction in liability or radiation exposure, or in increased protection to the environment.

Charge-back fees, where each generator pays for the costs associated with handling and disposal of its waste, can provide an incentive to reduce the generation of waste, but, each site should evaluate the charge-back system to determine its value in reducing waste for their own operation. Goals should be to provide a more equitable distribution of the cost of waste management, increase awareness of waste management costs, and provide incentives to programs to reduce the generation of wastes.

Compliance with Regulations and Orders:

This section should include the necessary compliance activities as required by the Federal, state, and local regulatory agencies.

For example, DOE Orders require a structured waste minimization program plan in place in May 1990, which will contain goals for minimizing the volume and toxicity of radioactive and hazardous waste.

Reporting:

A reporting system needs to be incorporated into the plan that fulfills the regulatory requirements which should include monitoring, auditing, and providing value engineering on existing processes. In addition, the reporting system, where practical, should establish cost accounting and cost/benefit analysis.

The routine reporting schedule under Order DOE 5400.1 is to coincide with the biennial reporting requirements under RCRA. The Implementation Guidance for DOE Order 5820.2A requires annual reporting on waste minimization activities.

CONCLUSION

Although waste minimization/reduction has been practiced at DOE sites for many years, it has only been recently that, because of the environmental and health legislation and DOE Orders, waste minimization/reduction programs and plans are being formalized.

Foremost of this legislation is the Hazardous and Solid Waste Amendments (HSWA) of 1984, mandates the reduction or elimination, as expeditiously as possible, the generation of hazardous wastes.

In concert with this legislation, DOE has issued policies and directives for waste minimization program: first, avoid as far as practicable the generation of hazardous wastes and reduce the toxicity of waste streams containing hazardous components; secondly, where wastes are unavoidably generated, recycle or reuse all or part of the waste stream components, and, finally treat non-reusable waste to further reduce the volume or toxicity.

Combined and cooperative efforts of waste generators, Federal and private industries, will be needed to eliminate/reduce generation of hazardous waste. National and international technology exchange programs will be needed to find environmentally acceptable solutions to the management of "mixed" wastes containing radionuclides and hazardous chemical components.

REDUCTION OF CHLORINATED SOLVENTS AT THE Y-12 OAK RIDGE PLANT

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Due to environmental and health problems, the future of chlorinated solvents appears very bleak. The Montreal Protocol, which has been signed by the United States, states that production of several of the Freons and Halons will be limited to 50% of the 1986 production levels by the year 1998. Several efforts are under way to change the terms of the Protocol to a total ban on production by the turn of the century or possibly sooner. The Environmental Protection Agency (EPA) has also announced its intent to add such solvents as methyl chloroform, several of the Freons not covered in the Protocol, and carbon tetrachloride to the terms of the Protocol as have several pieces of legislation proposed to Congress. Other chlorinated solvents such as perchloroethylene and methylene chloride have recently seen their threshold limit values lowered considerably by the Occupational Safety and Health Administration (OSHA). These solvents are widely used throughout industry so the increased regulation of them will lead to a total change in industrial operations.

The Oak Ridge Y-12 Plant has been actively seeking replacements for chlorinated solvents for several years. The first step in the reduction program was the identification of the solvents and their usages. The four main solvents used at the plant include Freon, methyl chloroform, perchloroethylene, and methylene chloride. The major use for these solvents was found to be for cleaning operations. These include such things as cleaning off machining coolant, general cleaning, cleaning of meter mix machines or foam spray guns, and metal chip cleaning and packing operations. Since 1985, the Oak Ridge Y-12 Plant has reduced its use of these chlorinated solvents from 89,000 gallons per year to 46,000 gallons per year.

The main reduction has been the use of perchloroethylene. Perchloroethylene was used as a machining coolant in the shops and was replaced with a mixture of propylene glycol, water, and borax. This reduced the amount of perchloroethylene being used from 81,675 gallons per year to 9,625 gallons per year. As with the implementation of any new process, there has been some problems with the change in coolant. The borax tends to precipitate out of solution forming solids on the equipment which has led to increased time in cleaning the machines. The propylene glycol has also caused some problems with removal of paint off the machinery. However, these problems are considered minor in comparison with working with perchloroethylene.

Other significant reductions have occurred in the area of changing out vapor degreasers which utilized perchloroethylene or methyl chloroform. These degreasers were replaced with ultrasonic cleaners which utilize aqueous detergent for cleaning. Ultrasonic cleaning consists of immersing a part in a liquid medium, agitating the liquid with high frequency sound, rinsing the part, and drying the part. The high frequency sound causes cavitation of the liquid medium on the surface on the area being cleaned. This cavitation is similar to a boiling action which creates a mechanical cleaning action on the surface.

Our studies have shown several factors to have an influence on the ultrasonic cleaning technique. These factors include the frequency obtained by the ultrasonic transducers, the liquid medium used in the ultrasonic system, and the coupling of the equipment with the cleaning medium. The optimum frequency level is dependent upon the cleaning application. If one is cleaning small electronic components or jewelry which can be damaged easily, a higher frequency (approximately 40 kHz) is required. If a good aggressive cleaning action is required such as with metal parts which have lubricants or oils on them, a lower frequency (approximately 20 kHz) is required. The lower the frequency, the greater the intensity of the radiating wave, thus the greater the cavitation intensity and the better the cleaning ability. In order to achieve cavitation, the frequency must be at least 18 kHz.[1] One drawback with these lower frequency levels is that the noise level increases as the frequency decreases. Therefore, with the lower frequency required for aggressive cleaning action, the noise level is irritating, necessitating ear protection for any operator near the ultrasonic unit.

The optimum liquid medium for use is also dependent upon the cleaning application. A liquid must be chosen which will clean the type of contamination present: organic, inorganic, or particulate. The liquid must also have good viscoelastic properties so that the proper cavitation can be achieved. Water has been shown to have excellent cavitation properties.[2] Cavitation can also be affected by the temperature of the liquid.

Due to the cavitation properties of water and the ability of detergents to clean several different types of contamination, aqueous systems are an excellent choice for use in ultrasonic cleaning. Several factors must be considered in choosing a detergent-based system. These include the type of emulsifier, type of wetting agent, type of corrosion inhibitors, and the cloud point of the detergent. The emulsifier must be able to disperse the dirt so that cleaning can take place. The wetting agent must reduce surface tension so that the surface can be wetted properly and the detergent will undercut the dirt. Corrosion inhibitors must be present in cleaning metals in particular to prevent corrosion of the parts being cleaned. The cloud point of a detergent indicates the effectiveness of the detergent. If a detergent begins to cloud, this is an indication that the detergent is no longer capable of cleaning as required. Clouding is dependent upon the temperature of the liquid medium. Thus, one must choose a detergent which will not cloud at the temperature which is required for cleaning. Figure 1 shows an example of the type of impact the detergent has on cleaning ability.

In this study, samples of type 304L stainless steel were contaminated with a low viscosity drawing lubricant. Several samples were flushed with or soaked in detergent "A" at 50°C. Several other samples received the same treatment with detergent "B" while other samples were vapor degreased using perchloroethylene. The samples were then analyzed using X-ray Photoelectron Spectroscopy (ESCA/XPS). This technique is capable of looking at several monolayers to partial monolayers on the surface of a sample. A ratio of the carbon to chromium peak heights obtained with the ESCA/XPS was then calculated. Figure 1 shows the comparison of these peak height ratios. The lower the carbon to chromium ratio, the lower the amount of carbon which is the major contaminant present on the surface of the material. Thus, the lower ratios indicate the cleaner surface. As one can see, the type of detergent used does have an obvious effect on the cleaning ability. As mentioned earlier, temperature has an effect upon the cavitation properties of a liquid medium. In using aqueous detergents, our work as indicated an optimum temperature of 50 to 60°C.

One other factor which can effect the cleaning ability of ultrasonic equipment is the coupling between the equipment and the liquid medium. Sometimes the equipment will have the proper frequencies for the type of cleaning required but the equipment will not couple properly with the liquid medium. This means that proper cavitation does not occur. This coupling can vary greatly between equipment brands. One test which is useful in comparing brands of ultrasonic cleaners is the aluminum foil erosion test.[1] This test consists of placing a piece of aluminum foil in the ultrasonic cleaner. If the cleaner is a low frequency cleaner capable of a good, aggressive cleaning action, holes will actually be chewed out of the aluminum foil. In testing different brands, one should design a series of tests similar to your cleaning needs to ensure the brand will meet your needs.

After taking these factors into account, our studies have indicated that ultrasonic cleaning is an effective means of cleaning metal parts. Figure 2 shows a comparison between vapor degreasing and ultrasonic cleaning. This study consisted of taking eight samples of uranium-6% niobium alloy and doing an initial cleaning on them to establish a baseline. The initial cleaning consisted of ultrasonically cleaning the samples for eight hours in a detergent, isopropanol, and demineralized water solution at 50°C, and thoroughly rinsing the samples in demineralized water. The samples were then fingerprinted and handled thoroughly in order to contaminate them. One sample was set aside as a control sample while the remaining samples were then dipped in a

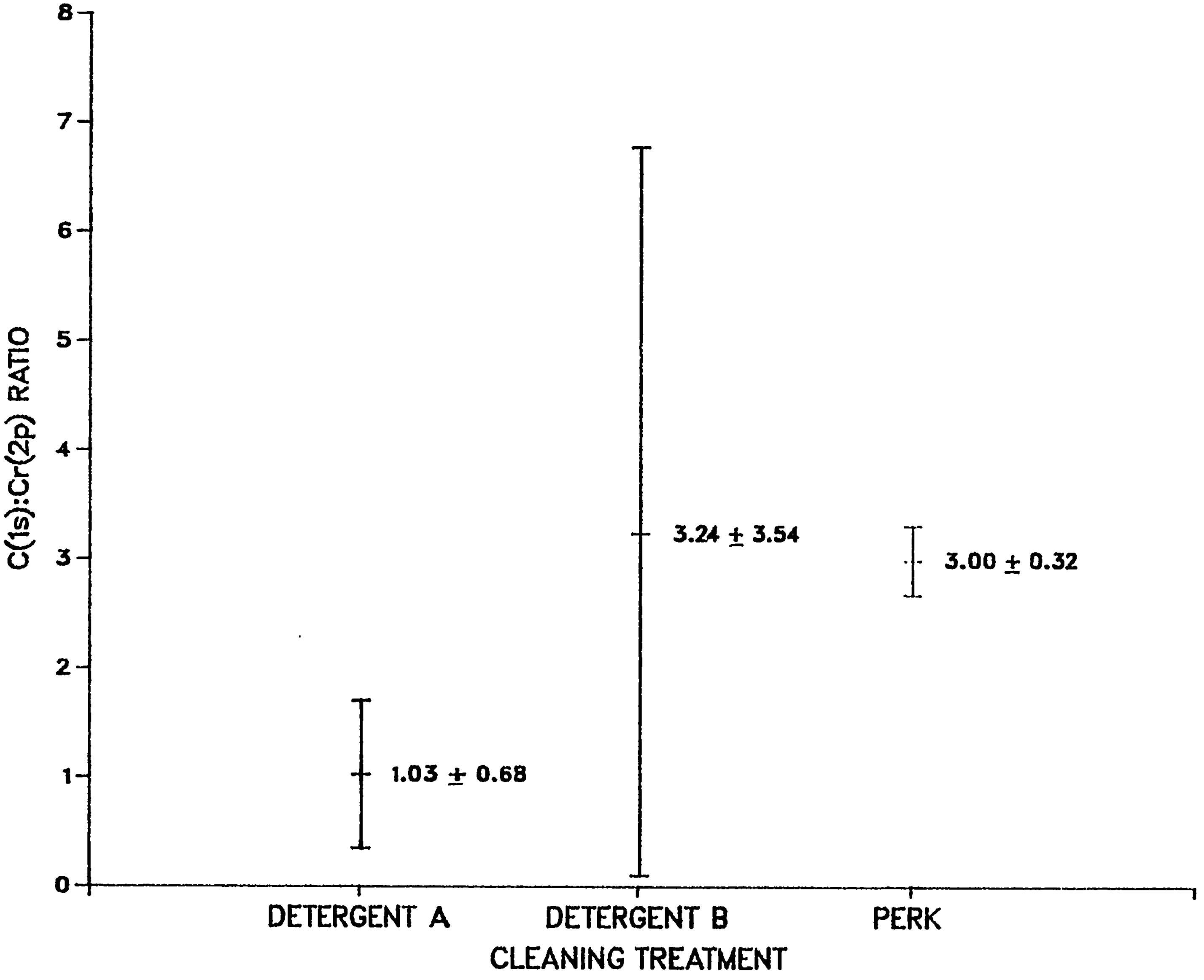

FIGURE 1 — IMPACT OF TYPE OF DETERGENT ON CLEANLINESS

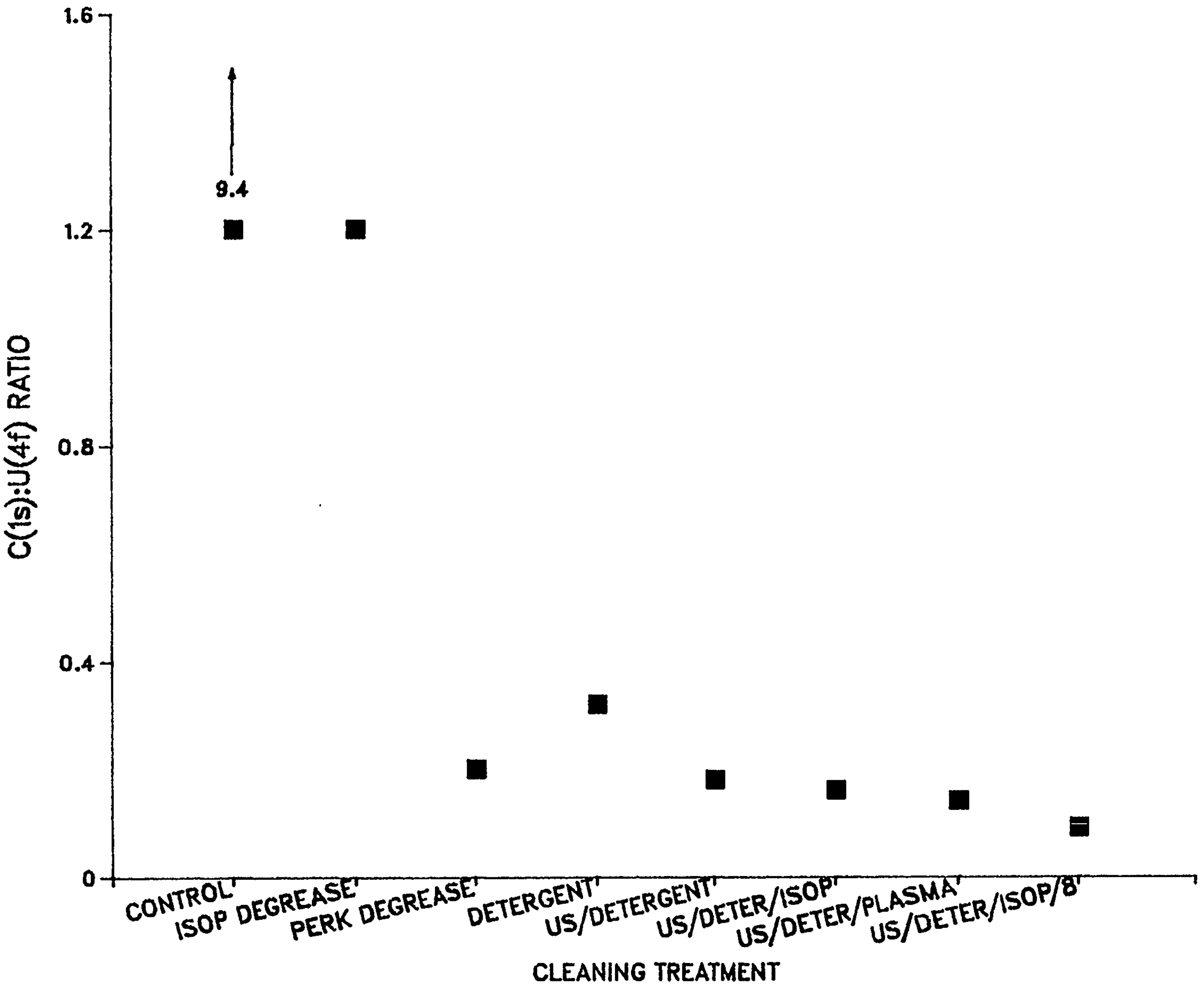

FIGURE 2 — EFFECTIVENESS OF CLEANING METHODS

rust-inhibiting oil and allowed to dry. Table 1 is a description of the treatments each of the samples received. After the treatment, the samples were analyzed using ESCA/XPS. From this data, the carbon to uranium peak height ratios were calculated. These are shown in Figure 2. As indicated before, the lower ratios indicate the cleaner surfaces. The ultrasonic cleaning techniques did much better than the isopropanol vapor degreasing and the detergent cleaning alone. These techniques also did slightly better than the perchloroethylene degreasing. One other lesson learned from this study was that the ultrasonic cleaning technique is only slightly better in its cleaning ability with extended periods of time rather than shorter periods of time. This study as well as actual parts cleaned in our production environment show a cleaning time of 20 minutes to be sufficient.

Ultrasonic cleaning has also been shown to have enough power to replace labor-intensive operations which utilized several different chemicals. Figure 3 shows a comparison between ultrasonic cleaning and a labor-intensive operation. In this study samples of type 304L stainless steel were formed using a drawing fluid, cleaned, and analyzed. The first set of samples was treated with drawing fluid "A" which is very difficult to remove, cleaned in an ultrasonic cleaner in a detergent solution at 50 C for five minutes, and rinsed ultrasonically in demineralized water. The second set of samples was treated with drawing fluid "B" which is somewhat easier to remove, cleaned in a labor-intensive operation which included hand cleaning in methyl chloroform, vapor degreasing in perchloroethylene, hand cleaning in acetic acid, and rinsing in demineralized water. The third set of samples was treated with drawing fluid "B", ultrasonically cleaned in a detergent solution for five minutes at 50°C, and rinsed ultrasonically in demineralized water. The ultrasonic cleaning technique used on the drawing fluid which was easier to remove yielded the cleanest surfaces and the most repeatable results. Thus, a labor-intensive operation which required using three different chemicals was replaced with ultrasonic cleaning with aqueous detergent.

In several cases, detergent cleaning alone was tried but did not suffice for our cleaning needs. The added power of ultrasonic cleaning was needed. Figure 4 shows a comparison between ultrasonic cleaning with detergent and detergent cleaning alone. In this study, five type 304L stainless steel samples were machined in a machining fluid and degreased in perchloroethylene. The first set of samples were maintained as control samples. The second set of samples were cleaned by immersion in a stirred bath of detergent "A" for 20 minutes at 55°C, rinsed under flowing water, and sprayed with acetone to aid drying. The third set of samples were cleaned in ultrasonic cleaner type "1" using detergent "A" at 74°C for four minutes, rinsed in flowing demineralized water, and sprayed with acetone to aid drying. The fourth set of samples were cleaned in ultrasonic cleaner type "2", using detergent "A" at 68°C for four minutes, rinsed ultrasonically in demineralized water, and sprayed with alcohol to aid drying. The

Table 1. Description of cleaning treatments for U-6Nb samples

Treatment	Description
Initial	All samples were cleaned ultrasonically for eight hours in 5 vol % detergent/20 vol % isopropanol/75 vol % demineralized water at 50°C. All samples were thoroughly rinsed in demineralized water.
Control	Fingerprinted and handled thoroughly.
Subsequent Treatment	After receiving the above treatment, the remaining samples were dipped in a rust-inhibiting oil and dried. They then received the following cleaning treatments.
Isop Degrease	Degreased for 30 min in isopropanol vapor
Perc degrease	Degreased for 30 min in perchloroethylene vapor
Detergent	Flushed for 20 min with 2 vol % detergent/ 98 vol % demineralized water at 40°C. Rinsed with demineralized water.
US/Detergent	Cleaned ultrasonically for 20 min in 2 vol % detergent/98 vol % demineralized water at 40°C. Rinsed.
US/Detergent/Isop	Cleaned ultrasonically for 20 min in 2 vol % detergent/98 vol % demineralized water at 40°C. Rinsed.
US/Detergent/Plasma	Cleaned ultrasonically for 60 min in 2 vol % detergent at 40°C. Rinsed in demineralized water, dried, and cleaned in argon plasma for 15 min.
US/Detergent/Isop/8	Cleaned ultrasonically for 8 h in 5 vol % detergent/20 vol % isopropanol/75 vol % demineralized water at 50°C. Rinsed.

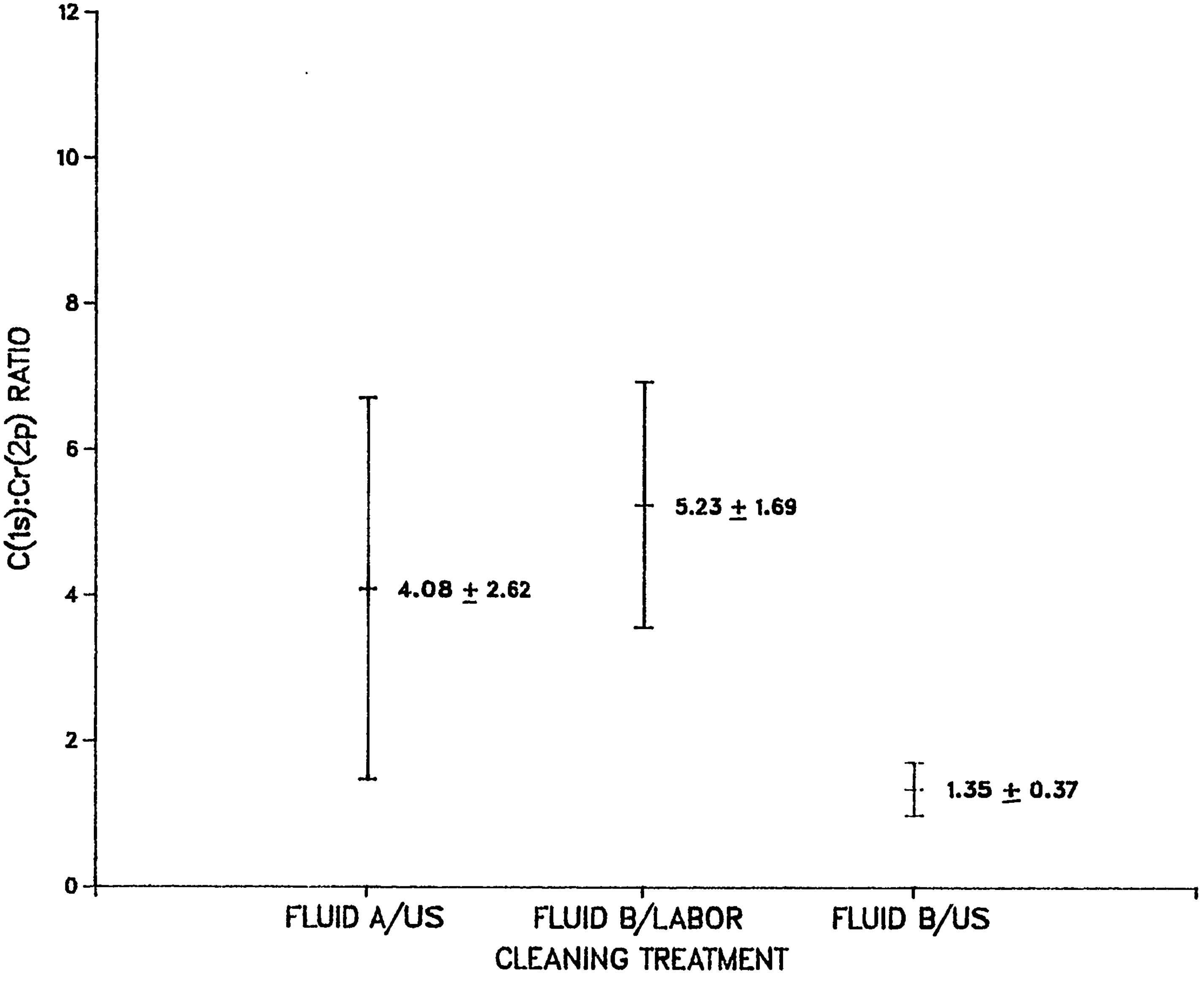

FIGURE 3 – COMPARISON OF ULTRASONIC CLEANING WITH LABOR INTENSIVE OPERATIONS

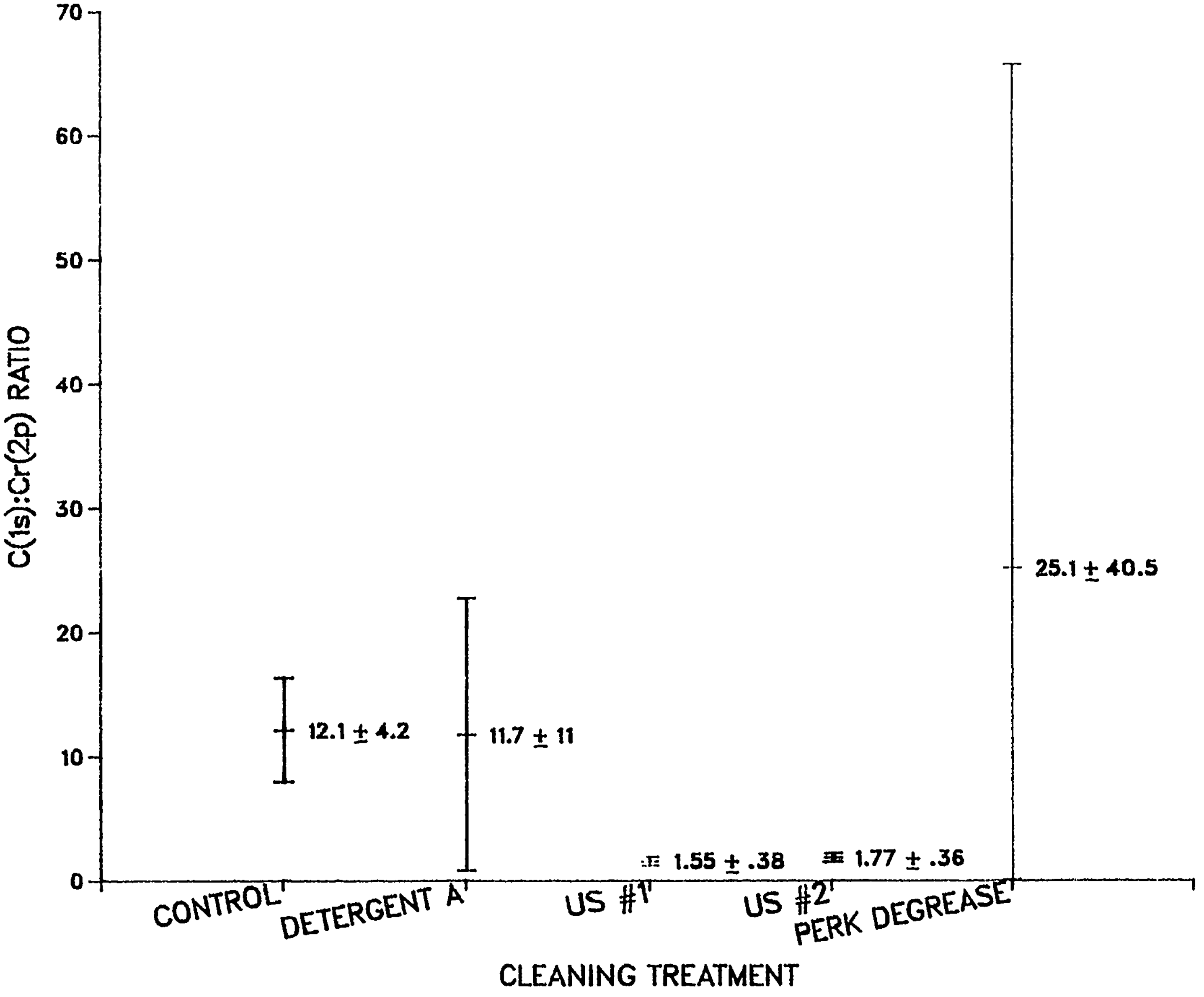

FIGURE 4 — COMPARISON OF ULTRASONIC CLEANING WITH DETERGENT CLEANING ALONE

fifth set of samples were vapor degreased an additional 20 minutes in perchloroethylene. These samples were then analyzed using ESCA/XPS and carbon to chromium peak height ratios were calculated. These ratios are shown in Figure 4. The ultrasonic cleaning technique again proved to be more consistent and effective than detergent cleaning alone and the vapor degreasing.

Ultrasonic cleaning has been proven as a good cleaning technique. The waste generated from this type cleaning can also be handled readily. Excess oil and trace metals are removed from the detergent solution which is then biodegradable.

There are disadvantages to ultrasonic cleaning. Unlike solvent cleaning operations where the solvent evaporates, the ultrasonic cleaning process requires a rinse step. This step requires additional equipment and time. Drying is also a factor to be considered following the water rinse. The equipment and initial set up for ultrasonic equipment can be very expensive which is yet another consideration. However, with the bans on production of several of the chlorinated solvents and the health risks and disposal problems associated with other solvents, the use of a water based system is attractive.

Currently, the work on reduction of chlorinated solvents is focused mainly on finding solvents which can be substituted for squirt bottle type applications. There are several problems associated with finding alternate solvents. The first problem is one of flammability. The factors which generally make solvents more effective also make them flammable. The only solvents which are nonflammable are the halogenated solvents or water. The halogenated solvents excluding the chlorinated solvents are generally very toxic or have health problems associated with them. Thus, one usually must turn to flammable solvents and handle them accordingly.

Another problem associated with alternate solvents is one of evaporation rate. The evaporation rate of chlorinated solvents is very fast (usually a matter of seconds). The only other solvents which have fast evaporation rates, e.g. acetone, alcohols, etc., are generally very flammable which we try to avoid. So in using a slow evaporating solvent, one must have a method of removing the solvent such as blowing dry or wiping dry.

Keeping these factors in mind, work has been conducted on finding effective solvents for many contaminants found in a machine shop environment such as machining coolant, lubricants, rust preventative oils, drawing fluids, and lapping oils. An extensive study has recently been completed on possible replacements for Freon used in cleaning off machining coolant. The machining coolant used in this instance is a water-based coolant containing such things as mineral oil and paraffin wax. Initially, possible replacement solvents were chosen using Hansen Solubility Parameter Theory.[3] According to this theory, a set of three parameters exist for each solvent and those solvents with similar parameters should behave similarly. An initial study was conducted with ten possible replacement solvents. Samples were initially cleaned ultrasonically to establish a baseline. These samples were soaked in the machining coolant and a controlled amount of solvent was used to clean off the coolant. These were then examined using ESCA/XPS. Of the ten solvents initially selected, six cleaned better than the Freon. Two of these solvents were eliminated from future consideration because of low flash points. The remaining four solvents (propylene glycol methyl ether acetate, ethyl lactate, dipropylene glycol methyl ether, and anisole) were then carried through a series of tests concerning three methods of drying: blowing dry with argon, chasing the solvent with alcohol, and wiping dry. In these tests several samples of type 304L stainless steel were initially cleaned ultrasonically in order to establish a baseline. These samples were coated with the machining coolant which was allowed to dry and flushed with a given amount of solvent being tested. They were then dried by one of the three methods mentioned above. One of these samples was also cleaned ultrasonically in order to compare this type of cleaning to solvent cleaning. The method of analysis used was the ESCA/XPS. The samples which were dried by blowing dry with argon yielded the worst results. This was probably due to contaminants being redeposited on the surface of the sample when the solvent was blown dry. The other two methods of drying yielded approximately the same results and appeared to be promising. The study was repeated using these two methods of drying. Figure 5 shows the results of the carbon to chromium peak height ratios obtained from the ESCA/XPS data on samples which were flushed with alcohol. Figure 6 shows the results of the peak height ratios for the samples which were wiped dry. The samples which were wiped dry yielded more repeatable and better results than the samples which were flushed with alcohol. This was probably due to the mechanical action of the wiping aiding in the cleaning. As one can also see, the possible replacement solvents also yielded as good if not better results than the Freon.

Several other concerns have to be addressed when looking at replacement solvents. One of these concerns is disposal. The possible replacement solvents mentioned above were all tested for biodegradability. This test was done using bacteria from the plant's Waste Coolant Processing Facility. The machining coolant used in these circumstances is biodegradable and is processed in this facility. If the replacement solvents in question are also biodegradable, then that would aid in waste disposal since Freon is not biodegradable. All of the possible replacement solvents were found to be biodegradable within a time frame of one to two weeks which would be acceptable turnaround for this facility.

Another concern is one of compatibility. The possible replacement solvents must be tested for compatibility with the materials on which

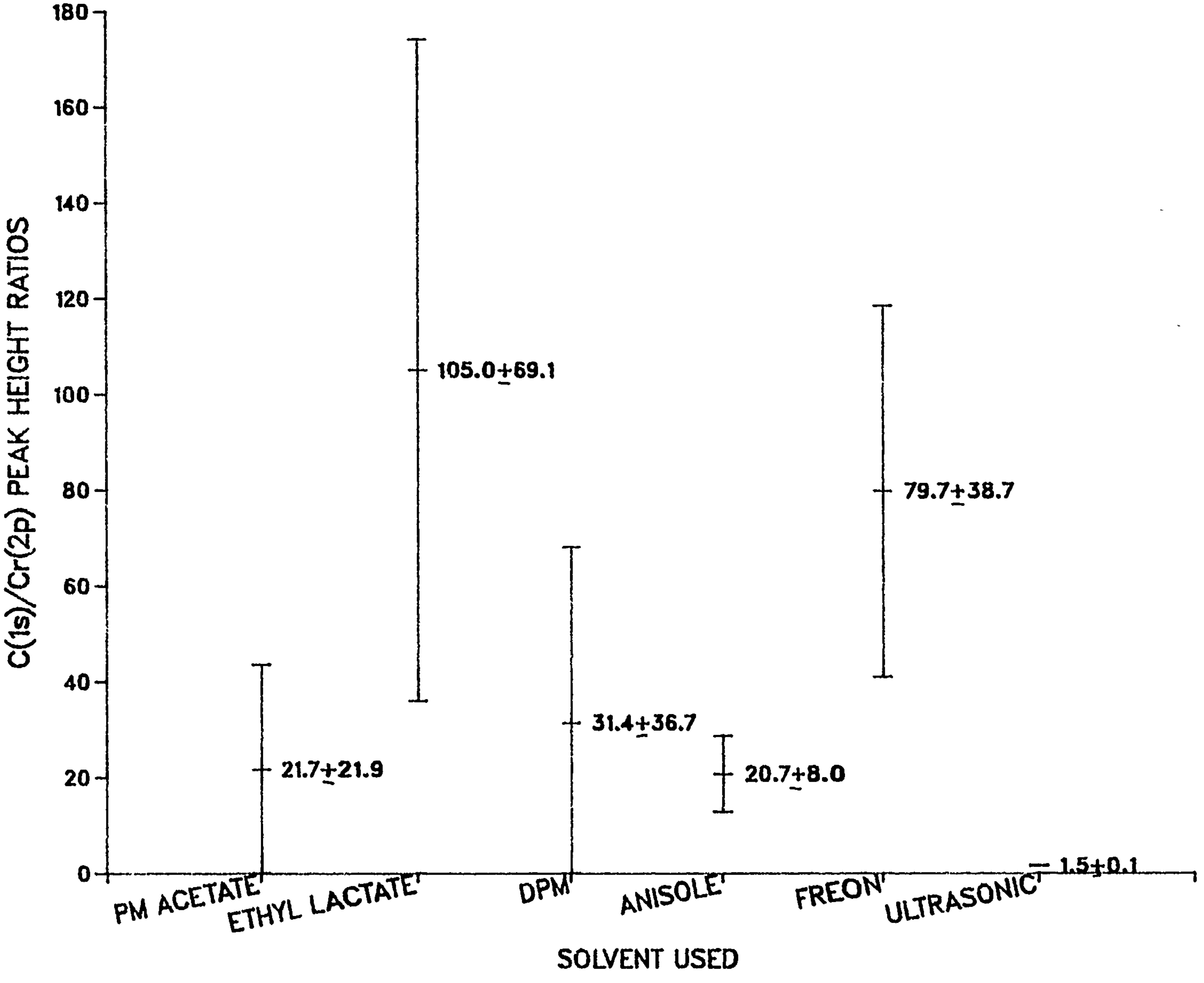

FIGURE 5 – CLEANING ABILITY OF SOLVENTS DRIED WITH AN ALCOHOL FLUSH

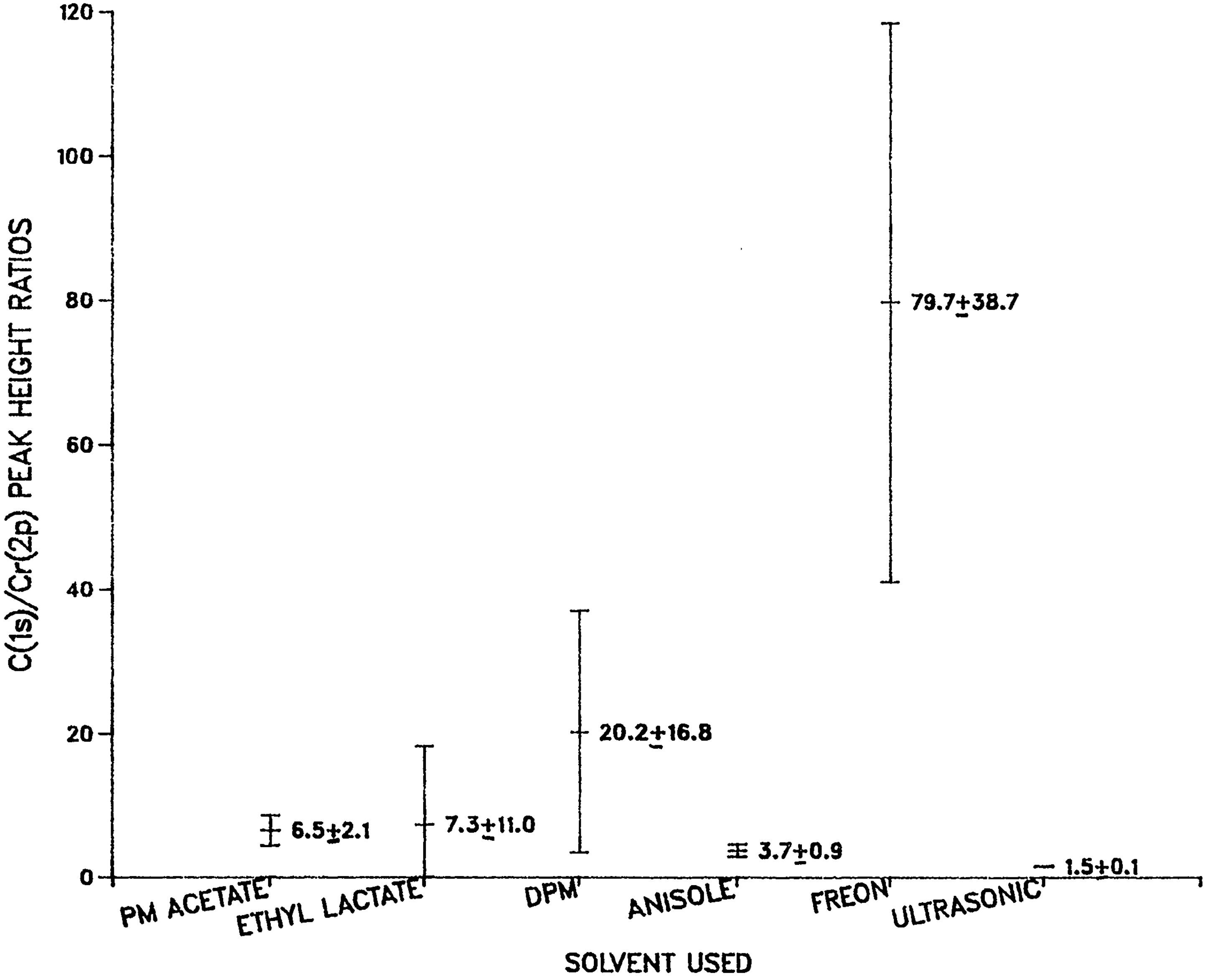

FIGURE 6 — CLEANING ABILITY OF SOLVENTS WIPED DRY

they would be used. In order to test the above solvents for compatibility, small metal samples of depleted uranium, uranium-6% niobium alloy, uranium-titanium alloy, AZ31B magnesium alloy, type 5083-0 aluminum, type 6061-T6 aluminum, type 7075-T651 aluminum, 4330V steel, HP 9-4-20 steel, type 304L stainless steel, and 15-5 PH stainless steel were immersed in each solvent for 72 hours. These samples were examined for surface defects or signs of corrosion. Of the above solvents, the only problems encountered with compatibility were that the anisole increased the amount of surface oxide on the depleted uranium and the ethyl lactate stained the surface of the AZ31B magnesium alloy.

One of the most important concerns to address is the health effects of the solvents. Each of the possible replacement solvents were examined by the Industrial Hygiene department and deemed to be safe for worker's use based upon the available data. A question has been raised concerning the dipropylene glycol methyl ether and a possible link to marrow toxicity.

Terpene based products have also become of major interest in recent years as possible substitutes for chlorinated solvents. A wide variety of products containing these solvents with detergents or surfactants exist on the market. There are some concerns with the use of these solvents. Most of these solvents must be followed by a rinse step. Our studies have shown that if the terpene based cleaners are not rinsed or removed properly, many of them form a very sticky residue which can bond surfaces together. There has also been some indication of material compatibility problems. The 72 day immersion test on one of the terpene based products showed severe oxidation on 4330V steel. There was also increased surface oxidation on all of the uranium alloys and the AZ31B magnesium alloy was severely stained. Compatibility with polyethylene squirt bottles has also been a problem with many of the terpene based products. The solvent tends to leach out the plasticizer causing the bottle to collapse. However, if you take these considerations into account, our studies have shown these solvents to be effective for rough cleaning of parts contaminated with oils.

Some of the more difficult to remove contaminants are the rust preventative oils and the lapping oils. Studies have been conducted with samples of type 304L stainless steel in order to find suitable solvents for cleaning these types of oils. The samples were initially cleaned ultrasonically to establish a baseline and then contaminated with the oils and allowed to dry. Given amounts of the solvents being tested were sprayed onto the surface of the samples and the samples were wiped dry. Some samples were also ultrasonically cleaned to compare that type cleaning with solvent cleaning. ESCA/XPS was used to analyze the surface cleanliness of the samples. Figure 7 shows the carbon to chromium peak height ratios for the samples contaminated with lapping oil. None of the solvents investigated did as well as the methyl chloroform or Freon in removing the lapping oil. The hydrocarbon solvent or mineral spirits did the best job of the replacement

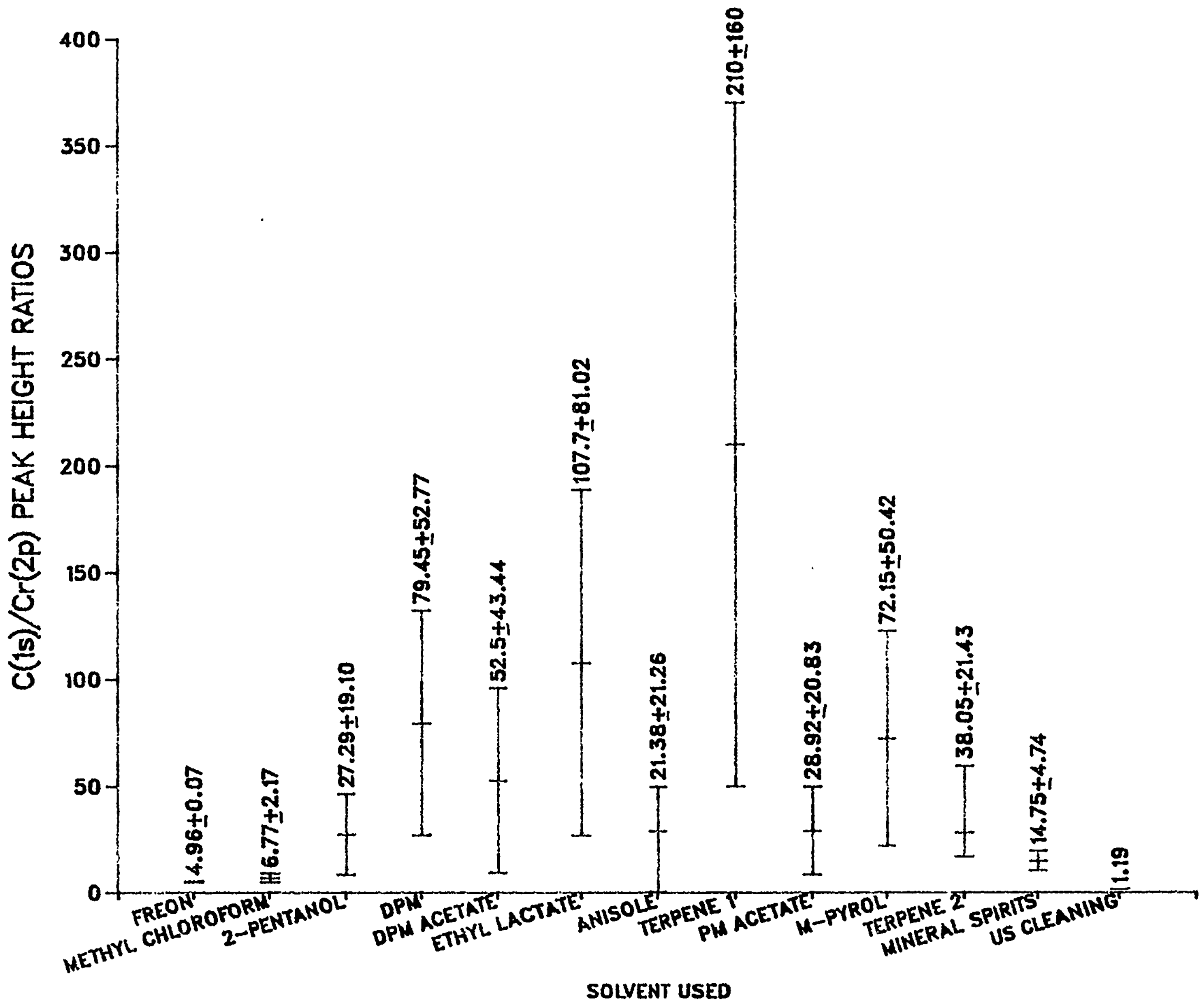

FIGURE 7 — REMOVAL OF LAPPING OIL

solvents. However, it could only be used for a rough cleaning. Once again ultrasonic cleaning was much better than the solvent cleaning. Figure 8 shows the carbon to chromium peak height ratios for the samples contaminated with the rust preventative oil. Methyl chloro-form yielded the best results. The Freon, n-methyl pyrrolidone, mineral spirits, and a terpene based product appeared to give similar results. However, the majority of the solvents were still so contaminated that the metal surface could not be detected by the ESCA/XPS. When conducting the tests, only the methyl chloroform, Freon, and mineral spirits appeared to be removing the oil readily. The remaining solvents seemed to soften the oil so that it could be wiped off. Again, ultrasonic cleaning gave much better results than the solvent cleaning.

The replacement of chlorinated solvents is a difficult task due to the wide variety of uses. Many of the usages must be examined individually and there is not one perfect solvent which would suffice as a substitute for all of the uses. Besides general surface cleaning and cleaning off machining fluids, these solvents are used for removing epoxies, paint removal, cleaning urethane spray guns, and as solvents in inks. We have had success in some of these areas and will continue our endeavor to find possible replacements for these solvents.

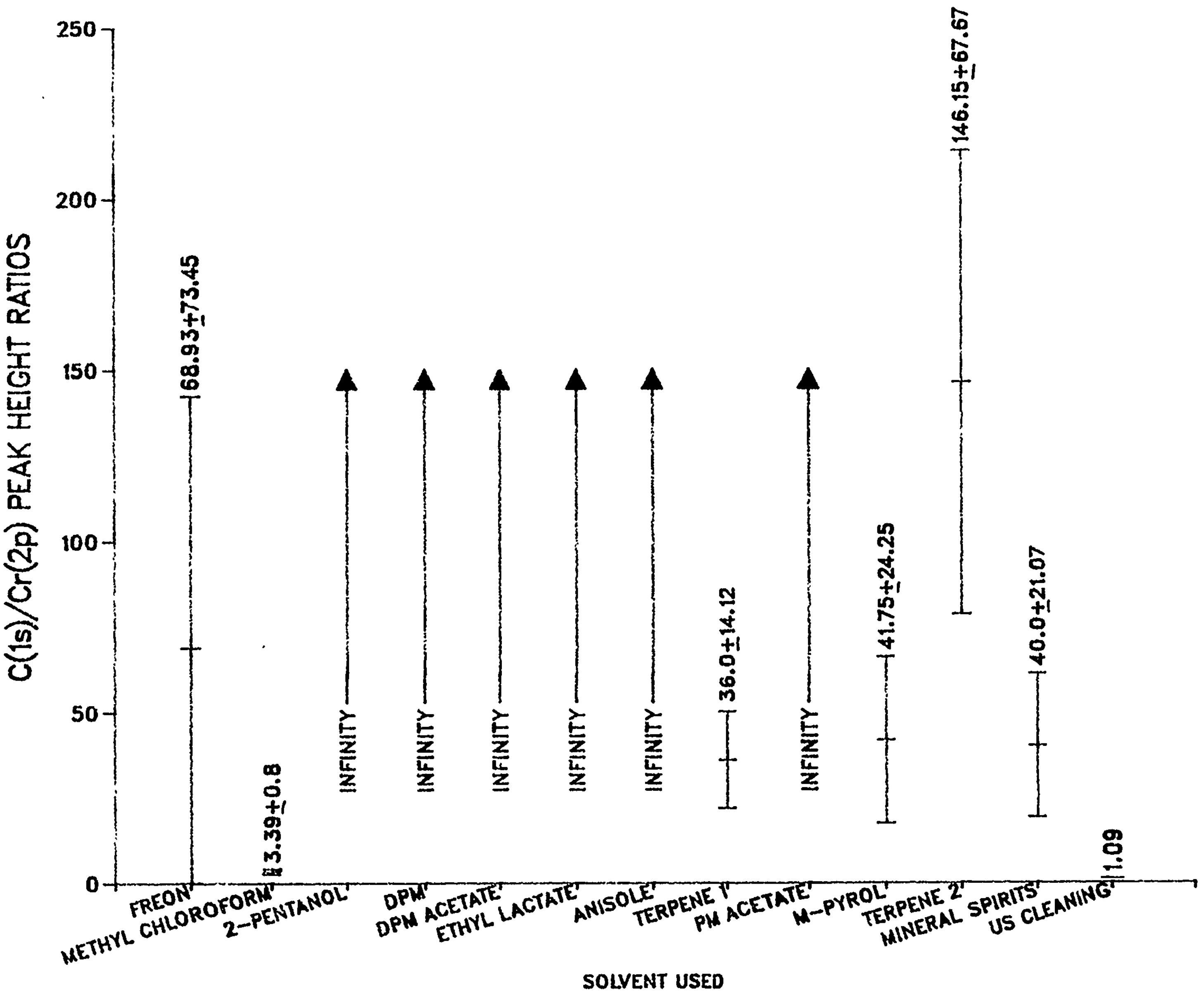

FIGURE 8 – REMOVAL OF RUST PREVENTATIVE OIL

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C-14 REMOVAL FROM SPENT ION EXCHANGE RESIN WASTES

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ABSTRACT

The presence of long-lived carbon-14 (half-life 5730 years) on spent ion exchange resins from nuclear generating stations makes disposal of the spent resin wastes difficult and costly. In heavy water cooled and moderated CANDU[1] reactors, the C-14 activities can be as high as 6 Ci/m^3 for spent ion exchange resins from the Primary Heat Transport purification system and 210 Ci/m^3 for spent resins from the Moderator purification system.

There are significant advantages in removing C-14 from the spent resins and immobilizing it for separate storage. Several methods for removing C-14 from spent resins have been evaluated experimentally. Acid stripping was found to be very efficient for C-14 removal. Extensive laboratory tests with simulated spent resins (ie, resins loaded with C-14 labelled chemicals) indicate that 98.5-100% of the C-14 can be removed. Results obtained so far with actual (station) spent resins indicate C-14 removal efficiencies over 99%. A pilot plant study is about to get underway.

Introduction

Carbon-14 is produced in nuclear reactors by neutron activation of oxygen-17, nitrogen-14 and to a lesser extent carbon-13. In CANDU reactors, it is produced mainly in the Moderator and Primary Heat Transport (PHT) systems, and also in the (nitrogen) Annulus Gas system. Because of its long half-life (5730 years) and the ease with which it is incorporated into living organisms, environmental release of C-14 must be minimized. However, control of C-14 emission from CANDU reactors is very effective. Over 90-95% of the C-14 produced is removed by the ion exchangers in the respective purification systems. The gaseous $^{14}CO_2$ is periodically released with purge gas from the moderator cover gas and the annulus gas systems. The $^{14}CO_2$ concentration in the purge gas can be significantly reduced by gas scrubbers or absorbers.[1,2,3,4,5] The actual C-14 emissions from

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[1] CANada Deuterium Uranium

the generating stations are minimal. For example, the annual total C-14 production of a CANDU 600 MW reactor is estimated[2] at 447 Ci/year for an 80% capacity factor, and the expected total C-14 emission is 10-20 Ci/year. This could be further reduced to about 1 Ci/year by adding appropriate control measures to the cover gas and annulus gas systems.

The large volumes of spent resin wastes generated in the purification systems have, however, created a waste disposal problem. The measured C-14 activity levels on the spent resins ranged from 0.2-6.4 Ci/m^3 for PHT spent resins and 47-213 Ci/m^3 for moderator resins [1,2,6]. The present practice of long term storage of the resins in engineered concrete structures is costly, at about $6,000 CDN per m^3. At Ontario Hydro, the annual resin requirement is estimated at 125 m^3 and is projected to reach 200 m^3 when Darlington Nuclear Generating Station (NGS) comes into service.

Removing C-14 from the spent resins and immobilizing it for separate storage will significantly reduce storage requirement for C-14 waste. The treated resins can be disposed as low or intermediate active wastes at a lower cost. Separating the C-14 from the resin wastes also offers the potential for C-14 enrichment to produce marketable isotope. However, the amount of C-14 produced would exceed the current world demand considerably. The primary objective of C-14 removal from spent resins currently remains to be one for efficient waste management.

In this work, several techniques for removing C-14 from spent resins were tested. The method of acid agitation was studied in detail. The results are encouraging and a pilot-scale study has been planned.

Review of Removal Techniques

Various techniques of resin stripping for C-14 removal have been reported in the literature. An acid stripping technique was investigated by Nott[7,8] with 2N HCl at room temperature using laboratory simulated spent resins. The C-14 removal efficiency, measured as the percent recovery in the NaOH absorbing solution, ranged between 62-96%. By addition of an ultrasonic probe to the resin column and air sparging to the recirculating acid, the recovery was improved to 92-100%. Speranzini and Buckley[9] heated simulated spent resins in air at 440-850°C and recovered 15-90% of the C-14 initially present on the resins. Bonnici et al[10] carried out several thermal stripping experiments and one acid stripping experiment. The removal efficiency varied considerably. They reported C-14 removal efficiencies up to 98% by thermal stripping of simulated resins with a stream of hot oxygen or nitrogen at 170-200°C. However, with actual station moderator spent resins, the observed C-14 removal was only 21-24%. Their acid stripping experiment using 2N HCl at 90°C on station moderator spent resins only yielded 14% C-14 removal.

Experimental

In the present work, spent resins were agitated in an aerated stripping solution. This set-up can be easily scaled up to operate as an agitated tank reactor with aeration.

A sketch of the laboratory apparatus is shown in Figure 1. Resin containing C-14 was mixed with a stripping solution (HCl, NaCl, Na_2CO_3 or NaOH) in a glass flask. The resin slurry was agitated by a magnetic stirrer. Air sparging was applied to purge the CO_2 evolved, and carry the off-gas through the system. A vacuum pump was used for drawing the off-gas through the system while maintaining a slight negative pressure within the system to avoid C-14 leakage. The average air purge rate was 135-150 mL/min. The water trap was acidified with HCl to 5% weight. The liquid sorbent used was 2N NaOH solution.

Several experiments were also conducted with acid fluidized columns. Here, acid solution and air were introduced from the bottom of the column to fluidize the resins. Magnetic stirring was not applied.

Laboratory simulated spent resin samples were prepared by equilibrating fresh ion exchange resins (Rohm and Haas Amberlite IRN 150) with a quantity of stock chemical solution of known activity level. The stock solution was prepared by diluting C-14 labelled $NaHCO_3$ or Na_2CO_3 (supplied by NEN/Du Pont and Amersham) with deionized water. The loading of activity on the resins was determined by liquid scintillation counting (LSC) of the solution before and after equilibration with the resin. Hionic scintillant (supplied by Canberra-Packard) was used.

The acid stripping technique was also evaluated using several spent resin samples retrieved from Ontario Hydro's Pickering NGS.

Results and Discussion [11,12]

I. Simulated Spent Resins

(A) Preliminary Results:

The preliminary results employing different types of stripping solutions are presented in Table 1. The removal efficiencies were measured by the percentage of the C-14 on the resins recovered by the absorbing solutions.

Agitating the resins in aerated HCl solution yielded the most promising results. The results in Table 1 show that high percent recoveries (92-99%) were obtained consistently by this method.

The high efficiency of the aerated acid agitation technique was probably attributable to the combined effect of air sparging and mechanical agitation. The CO_2 gas formed by the reaction of the acid with the carbonate/bicarbonate on the resins appears to have been effectively purged by the air bubbles. Any bubbles attached to the resins were likely separated by the mechanical agitation action. With the rapid removal of the gaseous CO_2 produced, the equilibrium of the chemical reaction

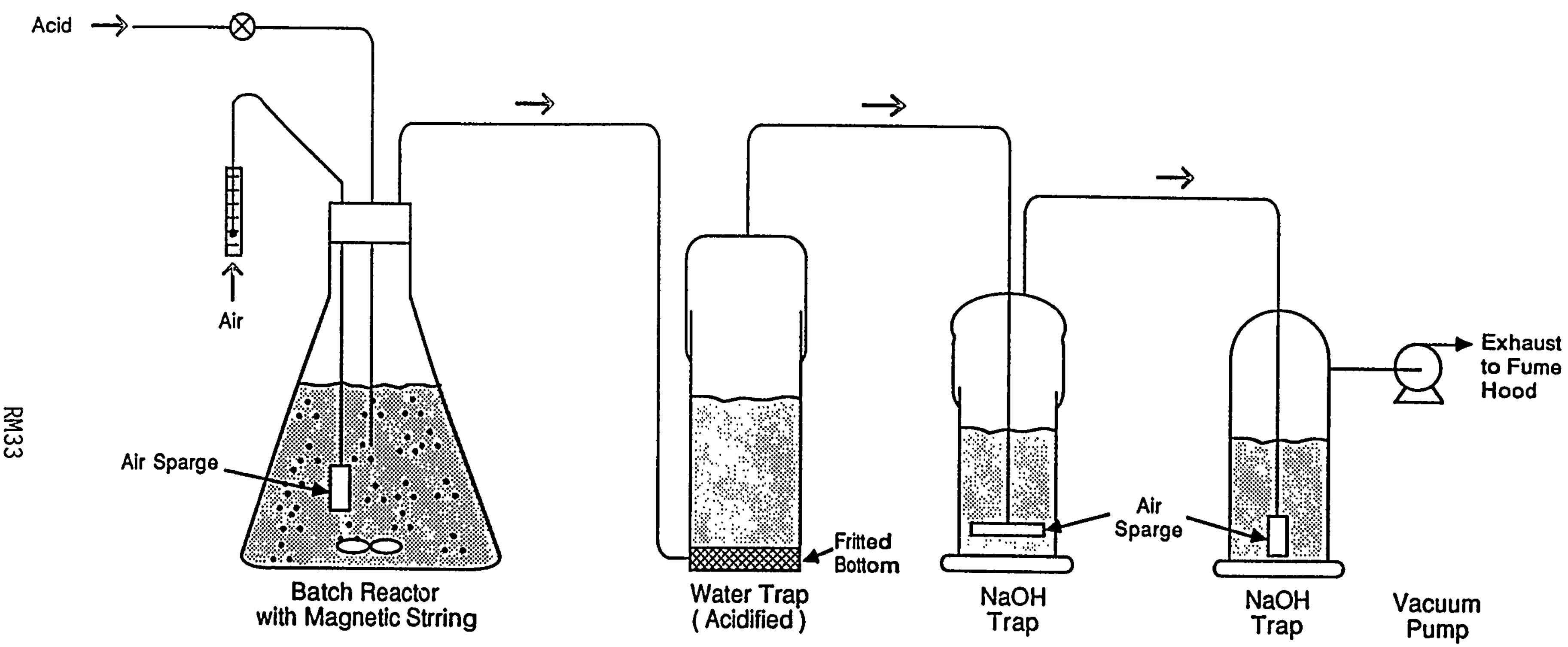

FIGURE 1. Apparatus for C-14 Removal by Acid Agitation

TABLE 1

Miscellaneous C-14 Removal Methods

(30mL of IRN 150 Resin with 50 Ci/m^3 C-14 loading)

RUN NO.	METHOD	REAGENT SOLUTION CONCENTRATION (N)	RUN TIME (min)	AGITATION SPEED (rpm)	AERATION RATE (mL/min)	SOLUTION VOLUME (mL)	PERCENTAGE C-14 RECOVERY (%)
1	Elution with Na_2CO_3	6	90	60	135	180	88.1
2	Elution with NaCl	6	90	60	135	180	19.3
3	Alkaline Stripping with NaOH	6	90	60	135	180	98.2
4(a)	Fluidization with HCl	3	90	-	400	480	93.9
4(b)	Fluidization with HCl	6	45	-	300	125	92.6
4(c)	Fluidization with HCl	6	90	-	0	125	96.8
4(d)	Fluidization with HCl	6	270	-	300	270	90.9
5(a)	Aerated Agitation in HCl	2	90	60	135	480	98.0
(b)	Aerated Agitation in HCl	3	90	60	135	480	92.5
(c)	Aerated Agitation in HCl	6	45	60	135	135	99.1

$$\overline{R.CO_3} + 2\,HCl = \overline{R.Cl_2} + H_2O + CO_2$$

is shifted in the forward direction.

The acid fluidization of resins using HCl solution involves the same chemical reaction, but the corresponding C-14 removal in Table 1 was lower. When the resins were acid fluidized without aeration, removal of the CO_2 produced was by diffusion alone. When aeration was introduced to purge the CO_2, the efficiency was further reduced. The gas bubbles tended to adhere to the resin beads and resulted in their floating together. This isolated the resin beads from reacting with the acid, and caused a lower removal efficiency.

It was concluded that the agitation of spent resins in aerated hydrochloric acid was the most efficient technique and a detailed evaluation was conducted as described below.

(B) Detailed Evaluation:

The consistency of C-14 removal by resin stripping with aerated HCl was evaluated by running replicate tests. An activity level of 50 Ci/m^3 was used which corresponds to the lower range of the activity levels (47-213 Ci/m^3) measured on moderator spent resins. The results and the statistical analysis of the data are summarized in Table 2.

Statistically, recovery efficiencies ranging from 98.5-100% can be claimed based on these results. Two-sided t-tests were applied. The hypothesis can be accepted at levels of significance of 99% for Type I error and 90% for Type II error.

Some additional results were obtained from experiments with resins preloaded to about 200 Ci/m^3 and the results are presented in Table 3. This activity level was closer to the maximum activity measured on moderator spent resins. The variables were varied slightly in a narrow range. The recovery was nearly complete in all cases.

II. Actual (Station) Spent Resins

Actual station resin samples were retrieved from the resin waste storage tanks of Pickering NGS. The resin waste was a mixture of spent resins from various sources. The C-14 activity in the mixture was relatively low but was adequate to represent that of the PHT spent resins.

Table 4 is a summary of the acid stripping results. In four (runs A-9,-10,-14,-15) of the fifteen experiments, the C-14 activity level on the resins was raised to about 200 Ci/m^3 by adding $Na_2{}^{14}CO_3$ (to approximate the maximum C-14 level measured on station moderator spent resins).

All the runs demonstrated C-14 removal efficiency over 99%. However, the significance of these percentage results requires some clarification. Unlike laboratory simulated spent resins, the total C-14 originally on the station spent resin samples was not known but was calculated by summing up the amounts remaining in the various solutions (spent acid, water trap and absorber traps) and on the treated resin after each experiment. It was assumed

TABLE 2

Statistical Evaluation

Experimental Conditions

Resin Volume = 10 mL of IRN 150
Acid Concentration = 6 N HCl
Acid Volume = 120 mL
Reaction Time = 45 minutes
Agitation Speed = 60 rpm

Results

Percent recovery of C-14 from simulated moderator spent resin ($50\ Ci/m^3$ loading of $NaH^{14}CO_3$ on IRN 150 resin) in 10 Trials:

(1) 99.90% (2) 100.02% (3) 102.20% (4) 98.56% (5) 101.46%
(6) 99.36% (7) 100.31% (8) 102.65% (9) 99.34% (10) 99.70%

Statistical Tests

Mean recovery efficiency : $\bar{x} = 100.35\%$

Sample standard deviation: $S = 1.3285$

Null Hypothesis Ho: Recovery efficiency, $U_o = 100\%$
Alternative Hypothesis H_A: $U_o \neq 100\%$

Student-t Statistic : $T_9 = \dfrac{(\bar{x}-U_o)}{S/\sqrt{n}} = 0.833$

$t_{9,0.005} = 3.25$

Since $T_9 < t_{9,0.005}$, therefore do not reject Ho.

TABLE 3

SIMULATED SPENT RESIN WITH HIGH INITIAL LOADING

(IRN 150 Resin Used per Run = 30 mL, Agitation Speed = 60 rpm)

Run No.	Experimental Conditions						Results									
							First Absorber		Second Absorber		Residual C-14					
											Spent Acid		Stripped Resin			
	Acid Conc. (N)	Acid Volume (mL)	Aeration Rate (mL/min)	Reaction Time (min)	C-14 Loading (μCi/mL resin)	Total C-14 Activity (μCi)	C-14 Recovered (μCi)	Percent Recovery (%)	C-14 Recovered (μCi)	Percent Recovery (%)	(μCi)	% of Loading	(μCi/mL)	Total (μCi)	% of Loading
S-1	0.5	125	135	225	204.86	6145.9	6175.5	100.48	3.80	0.06	0.19	.00	.001	0.03	0.00
S-2	2	58	100	225	204.86	6145.9	6283.2	102.23	2.35	0.04	0.17	.00	.002	0.06	0.00
S-3	6	98	100	225	204.86	6145.9	6193.7	100.78	2.56	0.04	0.20	.00	.002	0.05	0.00
S-4	6	125	135	45	240.49	7214.8	7371.8	102.17	0.41	0.01	0.35	.00	.000	0.01	0.00
S-5	6	125	135	45	240.49	7214.8	7182.7	99.55	0.16	0.00	0.04	.00	.000	0.00	0.00

TABLE 4

ACTUAL SPENT RESIN EXPERIMENTS

RUN NO.	SOURCE[1] RESIN	EXPERIMENTAL CONDITIONS[2]			C-14 RECOVERY						RESIDUAL C-14 ON STRIPPED RESIN			TOTAL C-14 ACTIVITY	
					Water Trap		First Absorber		Second Absorber						
		Resin Volume (mL)	Acid Conc. (N)	Acid Volume (mL)	C-14 Recovered (µCi)	Percent of Total (%)	C-14 Recovered (µCi)	Percent of Total (%)	C-14 Recovered (µCi)	Percent of Total (%)	Level of Residual C-14 (µCi/mL)	Total Residual C-14 (µCi)	Percent of Total (%)	Total C-14 Detected (µCi)	C-14 Loading on Resin (µCi/mL)
A-1	PI-447	10.0	6	120	0.002	0.01	18.53	99.51	0.00	0.00	0.009	0.09	0.48	18.62	1.86
A-2	PI-530A	10.4	6	120	0.002	0.00	97.36	99.33	0.36	0.37	0.028	0.29	0.30	98.01	9.42
A-3	PI-530B	10.4	6	120	0.002	0.00	93.41	99.48	0.26	0.28	0.022	0.23	0.24	93.90	9.03
A-4	PI-530C	10.0	6	120	0.002	0.00	71.33	99.15	0.30	0.42	0.031	0.31	0.43	71.94	7.19
A-5	PI-530C	30.0	6	140	0.033	--	324.07	--	0.02	--	NOT ANALYZED		—	≈324.12	≈10.80
A-6	PI-530A	32.0	6	135	0.023	0.00	319.85	99.70	0.01	0.00	0.029	0.93	0.29	320.81	10.03
A-7	PI-530A	30.0	2	135	0.019	0.00	309.10	99.75	0.01	0.00	0.025	0.75	0.24	309.88	10.33
A-8	PI-530A	32.0	2	135	0.042	0.01	337.51	99.66	0.01	0.00	0.034	1.09	0.32	338.65	10.58
A-9	PI-530B+ 5700µCi	30.0	2	135	0.761	0.01	5854.00	99.95	0.29	0.00	0.062	1.86	0.03	5856.91	195.23
A-10	PI-530B+ 5890µCi	31.0	6	135	1.589	0.03	6074.50	99.93	0.29	0.00	0.086	2.67	0.04	6079.05	196.10
A-11	PI-530B	29.0	6	135	0.085	--	260.13	--	0.01	--	NOT ANALYZED		—	≈260.23	≈8.97
A-12	PI-530B	29.0	6	135	0.165	0.06	260.90	99.53	0.01	0.00	0.036	1.04	0.40	262.12	9.04
A-13	PI-530B	31.0	6	135	0.031	0.01	276.27	99.34	0.01	0.00	0.058	1.80	0.65	278.11	8.97
A-14	PI-530B+ 5700µCi	30.0	6	135	0.585	0.01	5622.67	99.95	0.16	0.00	0.076	2.28	0.04	5626.70	187.56
A-15	PI-530B+ 5700µCi	30.0	6	135	0.236	0.00	5703.17	99.92	0.29	0.00	0.134	4.02	0.07	5707.72	190.26

[1] These refer to the sample tag numbers.
[2] Reaction time = 45 min., agitation speed = 60 rpm, aeration rate = 135 mL/min for all the runs.

that this sum represented adequately the total activity originally present on the resins; ie, activity balance was assumed to be maintained.

Small amounts of residual C-14 equivalent to less than 0.5% of the total C-14 were detected on the treated spent resins. The residual C-14 was probably present in some organic forms that do not react readily with HCl. When the stripped resins in runs A-8 and A-10 were further treated with a strong oxidizing agent, potassium persulfate ($K_2S_2O_8$), the residual C-14 was found to be essentially eliminated (only 0.007 Ci/m^3 remained in both cases).

During acid stripping, other radionuclides were also removed from the resins. The resins and the various solutions from runs A-7 and A-14 were monitored by gamma spectroscopy, and the results are presented in Tables 5 and 6. As expected, a significant fraction of the gamma-emitting radionuclides was found in the acid. A much smaller amount was carried over to the acidified water trap but no detectable quantities were found in the alkaline absorbers.

III. Ultimate Waste Disposal

The treated resin can be immobilized and disposed as (C-14 free) low level nuclear waste. The spent acid and water can be recycled and reused to the extent possible and then solidified and disposed.

The C-14 evolved in the off-gas can be absorbed in liquid sorbent and immobilized, or affixed on solid sorbents (eg. $Ca(OH)_2$) for long-term C-14 waste storage.

The net benefit is that by acid stripping the resin and affixing the CO_2 gas evolved on $Ca(OH)_2$ solid sorbents, the volume of C-14 waste can be significantly reduced. For resins with an initial C-14 activity of 200 Ci/m^3, the estimated volume reduction factor is 38 [12]. Immobilizing the treated resins and spent acid for disposal will result in a volume increase to approximately three times the original resin volume. The cost of disposing immobilized resin and acid as C-14 free waste is, however, much less than that for C-14 waste.

TABLE 5
ACID REMOVAL OF GAMMA ACTIVITIES (RUN A-7)
(30 mL of Sample PI-530A)

	BEFORE STRIPPING		AFTER STRIPPING									DISCREPANCY	
	RESIN		RESIN		ACID		WATER TRAP		FIRST & SECOND TRAP		TOTAL ACTIVITY	ACTIVITY DISCREPANCY	PERCENT DISCREPANCY
ISOTOPE	TOTAL ACTIVITY (µCi)	PERCENT UNCERTAINTY (%)	ACTIVITY ON RESIN (µCi)	PERCENT UNCERTAINTY (%)	ACTIVITY IN SOLUTION (µCi)	PERCENT UNCERTAINTY (%)	ACTIVITY ON RESIN (µCi)	PERCENT UNCERTAINTY (%)	ACTIVITY ON RESIN (µCi)	PERCENT UNCERTAINTY (%)	(µCi)	(µCi)	(%)
Co-60	14.76	3.0	5.91	0.3	3.20	0.4	0.001	17.8			9.11	5.65	38.3
Cs-134	0.78	6.0	0.36	2.6	0.21	2.7	-	-			0.57	0.21	26.9
Cs-137	4.65	3.0	2.22	0.7	0.95	0.7	-	-			3.17	1.48	31.8
Mn-54	0.33	7.0	0.15	5.4	0.09	4.1	-	-			0.24	0.09	27.3
Zn-65	1.05	1.60	1.47	1.7	0.05	15.1	-	-			1.52	0.47	44.8

TABLE 6
ACID REMOVAL OF GAMMA ACTIVITIES (RUN A-14)
(30 mL of Sample PI-530B)

	BEFORE STRIPPING		AFTER STRIPPING									DISCREPANCY	
	RESIN		RESIN		ACID		WATER TRAP		FIRST & SECOND TRAP		TOTAL ACTIVITY	ACTIVITY DISCREPANCY	PERCENT DISCREPANCY
ISOTOPE	TOTAL ACTIVITY (µCi)	PERCENT UNCERTAINTY (%)	ACTIVITY ON RESIN (µCi)	PERCENT UNCERTAINTY (%)	ACTIVITY IN SOLUTION (µCi)	PERCENT UNCERTAINTY (%)	ACTIVITY ON RESIN (µCi)	PERCENT UNCERTAINTY (%)	ACTIVITY ON RESIN (µCi)	PERCENT UNCERTAINTY (%)	(µCi)	(µCi)	(%)
Co-60	15.30	3.0	1.70	6.6	4.25	16.4	0.14	6.7	-		6.09	7.20	60.2
Cs-134	0.57	6.0	0.07	8.8	0.17	17.0	0.26	6.7	-		0.50	0.34	12.3
Cs-137	3.48	3.0	0.43	6.7	1.17	16.5	4.00	6.6	-		5.60	1.34	60.9
Mn-54	0.17	8.0	—	—	0.07	21.8	0.01	16.8	-		0.08	0.28	52.9
Zn-65	0.60	6.0	0.54	6.9	—	--	0.02	13.3	-		0.56	0.85	6.7

Note: Measurement results with percent uncertainty in excess of 20% were discarded.

Conclusions and Future Work

1. Essentially complete removal of C-14 from spent resins can be achieved by agitating the resin in HCl solution with air sparging. Minute amounts of residual organic C-14 may remain on some of the resins and an oxidizing step may have to be included.

2. The potential benefit of C-14 removal is an estimated volume reduction of C-14 waste by a factor of 38, with an associated volume increase of C-14 free low level wastes by a factor of about 3.

3. The experiments conducted with actual (station) spent resins were limited to low C-14 activity levels. Moderator spent resins with higher C-14 activity levels will be tested when suitable resin samples become available.

4. The effect of operating parameters, especially that of acid concentration should be studied.

5. A pilot plant with a capacity of 10 litres of resin per batch is under construction. A test program will commence shortly.

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PROTOTYPE LICENSING APPLICATIONS WORKSHOP

OVERVIEW OF THE EARTH MOUNDED CONCRETE BUNKER PROTOTYPE LICENSE APPLICATION PROJECT: OBJECTIVES AND APPROACH

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ABSTRACT

This paper presents an overview of the objectives and approach taken in developing the Earth-mounded Concrete Bunker Prototype License Application Project. The Prototype License Application Project was initiated by the Department of Energy's National Low-Level Waste Management Program in early 1987 and completed in November 1988. As part of this project a prototype safety analysis report was developed. The safety analysis report evaluates the licensibility of an earth-mounded concrete bunker for a low-level radioactive waste (LLW) disposal facility located on a hypothetical site in the northeastern United States. The project required approximately five person-years and twenty months to develop.

BACKGROUND

With passage of the Low-Level Radioactive Waste Policy Amendments Act of 1985, the Department of Energy (DOE) was given responsibility for providing technical assistance on alternative technologies for low-level radioactive waste (LLW) disposal. In early 1986, DOE's National Low-Level Waste Management Program (NLLWMP) initiated a project to develop conceptual designs and analyze six widely considered disposal concepts. These included: 1) shallow land disposal, 2) intermediate depth disposal, 3) below ground vaults, 4) above ground vaults, 5) earth-mounded concrete bunkers, and 6) modular concrete canisters. The project was completed in early 1987 and culminated with the issuance of DOE's Conceptual Design Report, "Alternative Concepts for Low-Level Radioactive Waste Disposal" and a national seminar on alternative technologies in July 1987.

It soon became evident that additional needs existed that could not be addressed by further developing the designs presented in the Conceptual Design Report. These needs, identified by representatives of several states and compact regions, focused on the licensing of LLW disposal facilities which incorporated disposal technologies other than shallow land disposal. Because eleven of the fourteen states then working toward the development of new LLW disposal facilities prohibited the use of conventional shallow land disposal it was apparent that this was an issue of general concern.

Licensing requirements for near surface disposal, that is disposal within the upper thirty meters of the earth's surface, have been in existence since the Nuclear Regulatory Commission (NRC) issued Title 10, Code of Federal Regulations, Part 61 (10CFR61), "Licensing Requirements for Land Disposal of Radioactive Waste" in 1982. Although the regulation was developed around the use of shallow land disposal, the NRC found that many alternatives could in fact be licensed under 10CFR61. It still, however, remained unclear if additional licensing requirements would be imposed when an alternative concept was employed. Both the DOE and the NRC agreed that a project should be developed to address these concerns and the Prototype License Application Project was conceived.

PROTOTYPE LICENSE APPLICATION PROJECT

Selection of Disposal Technologies

In planning this second major project on alternative disposal technologies, the NLLWMP provided for the development of two different alternative disposal concepts. It was felt that this approach would provide a broader perspective on the licensing of engineered alternatives, while furthering the development of two technologies for LLW disposal.

State and regional representatives were asked to provide recommendations for the two disposal concepts to be used as the basis for the project. Without a clear consensus, the NLLWMP chose two technologies which represented a broad spectrum of interests: below ground vault (BGV) and earth-mounded concrete bunker (EMCB) disposal. The BGV had been the technically preferred disposal concept of those representatives who attended the national seminar on alternative disposal technologies in July 1987. The EMCB, on the other hand, offered the most technical and regulatory challenges of the concepts considered. The EMCB provided additional advantages in that documented operational experience was available and many States were considering developing above grade vaults (earthen covered above ground disposal units) which are similar in design to the earthen tumulus which overlays a below ground concrete monolith.

Project Objectives

Four major project objectives were identified: (1) extend the available body of knowledge on alternative LLW disposal technologies, (2) identify and address potential licensing issues associated with alternative disposal technologies, (3) provide for NRC review and comment on the disposal technology design, safety analysis, and licensing issues, and (4) develop prototypical licensing documentation using existing NRC guidance. These objectives most directly addressed the concerns which had been related to DOE by state and regional representatives. It was determined that the four project objectives could best be satisfied by the preparation of a prototype Safety Analysis Report (SAR) following the guidance provided by the NRC. Although an actual license application additionally includes an Environmental Report (ER), only a prototypical SAR was developed.

Approach

A request for proposals was issued in early 1987. Rogers and Associates Engineering Corporation and Ebasco Services Incorporated were selected to conduct the BGV and EMCB projects respectively. The selection of two contractors allowed both concepts to be developed concurrently thus expediting the schedule in support of State needs. The use of independent contractors would additionally allow two different approaches to be developed and submitted to the NRC for review.

In an effort to coordinate the development of the two projects and provide a basis of comparison between the prototypical SAR's a set of initial conditions were developed for use by both contractors, these included: (1) annual disposal volume of 250,000 cu ft, (2) operating facility life of 30 years, and (3) a hypothetical location in the northeastern United States. Both contractors were additionally instructed to utilize the previously released Conceptual Design Report as a point of departure in developing the disposal unit designs. By design, the specified disposal volume and operating life are consistent with the design basis conditions of the Conceptual Design Report. The northeastern United States was selected as the geographical location for the site since it was thought to provide many technically challenging features including a relatively depth to the water table and high annual precipitation.

The NRC's "Standard Format and Content of a License Application for a Low-Level Radioactive Waste Disposal Facility" (NUREG 1199) and "Standard Review Plan for the Review of a License Application for a Low-Level Waste Disposal Facility" (NUREG 1200) were specified as the basis for format of both reports. In accordance with these documents, the following major elements were identified: (1) general information, (2) site characteristics, (3) design and construction, (4) facility operations, (5) site closure and institutional controls, (6) safety assessment, (7) occupational radiation protection, (8) conduct of operations, (9) quality assurance, and (10) financial assurances.

Due to project constraints, including the hypothetical nature of the study, it was necessary to limit the scope to those items which most directly supported the project objectives. Therefore, emphasis was placed on the disposal unit design and those areas which supported the review of the design. Ancillary design features, such as the administration and support buildings were de-emphasized while the disposal units were developed to a level of detail necessary to meet the intent of the licensing requirements.

In the development of a "real" license application, the performer would have a considerable amount of data available on both the waste stream and characteristics of the site. Although initial conditions were generally specified (above), it was necessary for both contractors to develop a hypothetical waste stream and site to a level of detail necessary to support the licensing analysis (performance assessment). Emphasis was placed on developing, evaluating and selecting data, which although hypothetical, was representative of those facilities currently being proposed.

Both contractors were additionally directed to address those items which had been identified by State representatives as major issues related to the licensibility of engineered alternatives for LLW disposal. These included but were not limited to: (1) the timeframe over which a performance assessment should be conducted, (2) the use of engineered barriers for intruder protection, (3) the minimum distance required between the aquifer and the bottom of the disposal unit, (4) implementation of the U.S. Army Corps of Engineers recommendations for engineered alternatives, 5) the use of representative performance assessment "system" codes for conducting licensing analyses, (6) a methodology for providing for long-term stability, (7) demonstration that an engineered alternative does not degrade the natural performance of the site, and (8) the amount/quality of information necessary to meet the licensing requirements.

Deliverables

Work on both projects was initiated during the third quarter of 1987. Upon completion of two independent technical reviews and an exhaustive peer review by State representatives, deliverables from both projects were finalized in October 1988. The final Prototype Safety Analysis Reports were concurrently submitted to the NRC for review and distributed to representatives of host States and Regional Compacts in November 1988.

NRC REVIEW AND FUTURE ACTIVITIES

The NRC has recently completed a review of the EMCB Prototype Safety Analysis Report. As previously agreed upon, the review focused on the design of the engineered alternative disposal concept. Review of the BGV Prototype SAR has recently been initiated by NRC staff. A second licensing workshop will be conducted upon completion of that review. The date for the second workshop has not yet been set.

CONCLUSION

The importance of the Prototype License Application Project does not rest in the results of the analysis, the comparison of the selected disposal concepts, nor the "representativeness" or completeness of the information which is presented. Rather, the importance and significance of the Prototype License Application Project results from the approach taken in meeting the LLW licensing requirements and the NRC's evaluation of that approach.

It is additionally important to note, that in developing an approach both contractors were directed to address those items which had been identified by State representatives as major issues related to the licensibility of engineered alternatives for LLW disposal. The approach taken for this exercise should not be construed to represent the preferred approach but an attempt to try and resolve some of these perceived outstanding issues.

Although the work performed by Ebasco Services and Rogers and Associates represents a significant accomplishment, it has been estimated that this accounts for approximately one sixth of what is required to support a "real" license application. Considering that both projects each required approximately twenty months and a five person-year effort to develop, and the NRC expended another two and one-half person-years in conducting the mock licensing review, it is apparent that there is still alot of work yet to be done by developers and regulators alike.

ADDITIONAL INFORMATION

Additional information and copies of both documents are available to representatives of states or regional compacts by contacting Ms. Berlinda Morreale, NLLWMP, EG&G Idaho, Inc., (208) 526-0511. Other agencies or organizations may obtain copies by contacting National Technical Information Service (NTIS) at (703) 487-4650 and referencing the following reports.

DOE/LLW-72T	Prototype License Application: Safety Analysis Report Below Ground Vault
Vol I	Safety Analysis Report, October 1988
Vol II	Safety Analysis Report Appendices A - H, October 1988
Vol III	Sensitivity Analysis Report, October 1988
Vol IV	Measurements of Concrete Properties for LLW Disposal Facilities
DOE/LLW-73T	Prototype License Application: Safety Analysis Report Earth Mounded Concrete Bunker
Vol I	Safety Analysis Report, November 1988
Vol II	Safety Analysis Report Appendices, November 1988

EARTH-MOUNDED CONCRETE BUNKER PLAP TECHNICAL APPROACH

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INTRODUCTION

Under the US DOE Prototype License Application Project (PLAP) (1), Ebasco Services Incorporated was commissioned to develop a preliminary design of the Earth-Mounded Concrete Bunker (EMCB) concept for low-level radioactive waste (LLW) disposal (2). The EMCB disposal concept is of great interest because it represents the only engineered LLW disposal technology currently in use in the commercial sector (3). By definition, the EMCB disposal structure is located partially below grade and partially above grade. The concrete bunker is an engineered structure designed to be structurally stable for the prerequisite time horizon.

The basic design parameters of the disposal facility were stipulated by US DOE, a northeast site location, representative waste, 30 year operational life, and a 250,000 ft^3/year disposal capacity. The design was developed to satisfy only US NRC Part 61 (4) disposal requirements, not individual state requirements that may go beyond Part 61 requirements. The technical safety analysis of the preliminary design was documented according to the format specifications of NUREG-1199 (5), to the extent practicable with quite limited resources.

DESIGN PHILOSOPHY

To develop a cost-effective design, Ebasco chose to segregate the disposal of LLW by its waste classification (Part 61.55). By segregating the waste according to its Part 61 waste classification, the allocation of engineering resources was thought to be optimized. Ebasco chose a 100-year design life criterion for the Class A waste disposal structure and a 500-year design life criterion for the more hazardous waste, i.e., classes B and C waste. To assure the long-term integrity of the class B/C waste structure, the structure was generally designed in a manner consistent with the recommendations of the Army Corps of Engineers (6).

The disposal system is designed to have modular disposal units to permit interim closure of each unit as it is filled. Each disposal unit is individually monitored and incorporates a water collection and leak detection system. This modular feature facilitates potential remediation of the disposal unit or waste recovery efforts. The individual Class A disposal units are sized to the expected Class A waste volume to permit the frequent interim closure of units. The engineered soil cover is a multi-layered system designed with redundant features to prevent water infiltration into the disposal units.

The individual disposal units are constructed sequentially (as needed) in a planned cluster. When an entire cluster is completely filled with waste, the permanent (multi-layer) cap is constructed over the entire cluster.

FACILITY DESCRIPTION

For purposes of this study, the site was assumed to meet all the site suitability requirements of Part 61.50(a). To illustrate the practical aspects of engineering, a hypothetical site location in the northeast was chosen, see Figure 1. The site is located in a rural area, with 9000 persons residing in a 10 km radius. The site is situated between two intermittent streams (1.6 km to the east and 1.6 km to the west), and 20 km west of a major river. Access to a state highway is available 0.4 km from the site. The meteorological conditions are typical of the northeast. The site strata has the following composition: recent alluvium (2 ft thick), glacio-fluvial soil (20 ft), lacustrine clay (65 ft), weathered rock (3 ft), shale (100 ft), and silty sandstone (100 ft). The water table is located at the 90 ft depth. The local site topography is shown on Figure 2 with 20-ft contour lines.

The disposal facility is situated on a site of 165 acres. The restricted area for disposal operations occupies 65 acres, surrounded by a buffer zone, 500 ft wide. The disposal facility (Figure 3) consists of eight EMCB clusters, four clusters for Class A waste and four clusters for Class B/C waste. The proposed facility design has all the necessary facilities to support the waste disposal operation, including: (a) temporary waste storage building, (b) administration building, (c) access control building, (d) truck wash and inspection station, (e) maintenance building, and (f) retention ponds. A description of the key (and unique) design features is provided below.

Disposal Units For Class A Waste

The EMCB for Class A waste is shaped like a truncated pyramid, see Figure 4. The engineered structure for the EMCB cluster is 360 ft. square and 28 ft. high. The structure consists of a 15 ft. high tumulus above a 13 ft.-high concrete vault. The concrete vault is completely filled and acts as a foundation for the tumulus. Each large EMCB cluster has a disposal volume for 9 years of Class A waste. To provide the facility with 30 years of disposal capacity, the facility was designed with three large clusters and one small cluster.

The concrete vaults lay on a gravel drainage bed. The vault has 3 ft. thick concrete walls supported by concrete footings. The vault interior is partitioned into 60 ft. x 60 ft. disposal compartments with precast concrete block walls. The precast concrete blocks are 3 ft. high, 3 ft. wide, and 6 ft. long. The interior concrete partition walls lay on concrete footings. The vault is backfilled with concrete. When a compartment is filled, a 1 ft. thick concrete slab (with rebar) is installed over the vault compartment.

When the vault portion is completely filled (4.5 years), waste emplacement in the tumulus begins. The lower portion of the tumulus is backfilled with sand and the upper portion is backfilled with concrete. As each compartment of the tumulus is completed, it is capped with a 0.5 ft. thick concrete cap. When the entire tumulus is completely filled (4.5 years), an engineered interim cover system is installed over the disposal structure. The specified construction material is concrete made with Type II cement.

Disposal Units for Class B/C Waste

The EMCB for Class B/C waste is a concrete vault, partially below-grade and above-grade, see Figure 5. The vault is approximately 100 ft. square and 20 ft. high. The Class B/C vault is modular, similar to the Class A vault. The Class B/C vault has a concrete floor and lies on a gravel drainage bed. The vault has 3 ft. thick exterior and interior concrete walls. The interior walls partition the EMCB into 25 ft x 25 ft disposal compartments. All walls rest on concrete footings. The vault is backfilled with concrete. When a compartment is filled, a 1 ft. thick concrete slab (with rebar) is installed over the vault. When the entire vault is completely filled (8 years), an engineered interim cover system is installed over the disposal structure. The specified construction material is concrete made with Type II cement.

Covers

When each concrete structure is completely filled with waste, an interim engineered cover is immediately installed over the concrete structure. Figure 6 presents the details of the engineered cover. A 6 ft. thick cover is installed over Class A EMCB while an 8 ft. cover is installed over a Class B/C EMCB. The final site cover (at site closure) adds another 2 ft. of soil above the interim cover.

Above the concrete structure, the slope of the cover is 2 percent. Off the concrete structure, the slope of the cover is 5:1 (horizontal:vertical). The cover surface is stabilized with native grass vegetation.

Surface Water Control Features

The facility's surface water drainage system has several elements. Off-site water is directed away from the disposal facility by a drainage ditch and berm surrounding the facility. The design is consistent with the natural topography of the site.

The on-site drainage system is designed to direct water flow away from the disposal units and leave the facility by gravity, consistent with the site topography. During operations, any precipitation falling in a disposal unit is directed to a retention pond, where the water is sampled. If the water is found to be contaminated, it is treated prior to being released.

At site closure, the entire site is covered with additional soil and regraded to minimize flow velocities and prevent water erosion. The drainage ditches have a 6-in sand bed with a 1-ft thick riprap liner.

The drainage system is designed to handle a 100-year storm. If a worst kind of storm (i.e., PMP) occurs, no structural impact to the vault is expected to occur. Temporary flooding is not expected to lead to irreparable damage. During the operational period and the 100-year active institutional care period, repair to the drainage system is readily available. After the 100-year active institutional care period, the Class A EMCBs are not as important because the Class A waste has significantly decayed. The Class B/C EMCBs are fully expected to withstand the PMP without any significant release of radionuclides. Even if the top portion of the engineered cover is eroded, the bottom portion is expected to remain. As a last resort, the concrete roof is expected to remain intact.

Intruder Barrier

The human intruder barrier for the Class C waste is the concrete vault, which is backfilled with concrete. The roof of the vault is a 1-ft thick concrete slab (with rebar). The specified construction material is concrete with Type II cement. The engineered cover has a cobble layer to deter biointrusion. Since Class C waste may be located less than 5 m from the surface, the explicit engineered intruder barrier is required to have an effective life of 500 years.

Site Utilization Plan

Figure 3 shows a general arrangement of the disposal facility. An access road is constructed to connect the facility with the nearest state highway. The administration building and support facilities (e.g., power distribution, well water treatment, sanitary treatment, parking lot) are located outside the fenced-in and guarded restricted area. All personnel and vehicle access to the restricted area is through the front gate. The truck inspection station/truck wash is located just inside the gate. The front gate is controlled from the Access Control Building. Construction trailers are located adjacent to the Access Control Building.

Other support facilities include the equipment storage area, equipment maintenance building, waste water treatment, two evaporation/retention ponds, soil pile, and the temporary waste storage building (TWSB).

The clusters are separated by a minimum of 130 ft from each other and the site road system. This separation distance will assure that completed disposal units are not disturbed by ongoing disposal operations at nearby active disposal units. The facility's road system is constructed in phases, in parallel with the development of the EMCB clusters. The site drainage system is developed in parallel with the road system.

Completely surrounding the active disposal area is a perimeter berm and ditch to divert off-site precipitation from running on-site.

Temporary Waste Storage Building

The TWSB provides separate facilities to store both high activity and low activity waste. The primary function of the TWSB is to store high-activity waste until it is convenient to conduct waste disposal operations. Low activity waste is disposed of immediately upon arrival. However, the TWSB does have a two-week storage capacity for low activity waste in the event of a site contingency. The nominal design storage capacity for high-activity waste is two months. In addition, the TWSB has the capacity to repackage certain defective waste packages.

The high activity portion of the TWSB is constructed with a minimum of 2-ft thick concrete walls. The remaining portion of the building is constructed with sheet metal.

DISPOSAL OPERATIONS

All waste shipments are scheduled for convenience of the disposal operation. Upon arrival, shipments and waste manifest are inspected and checked for compliance. Normally, Class A waste are directed immediately to the disposal unit. Waste emplacement of Class A is conducted continuously in a planned sequence. Certain characteristics of the waste form affect their placement in the disposal unit. High activity waste are preferentially placed under low activity waste to minimize worker exposure. High-density waste are distributed evenly across the floor of the disposed unit to minimize differential settlement of the disposed unit. The emplaced waste is backfilled with concrete in the vault portion. In the tumulus, granular sand is used to backfill the lower portion of the tumulus, while concrete is employed in the upper portion.

Due to the limited amount of Class B and C waste, its disposal is performed as a batch process. Such waste may be stored in the TWSB until sufficient volume is accumulated to complete the emplacement and backfill of an entire waste layer. Concrete is the backfill material in the Class B/C unit. Provisions to minimize worker exposure include the use of: (1) concrete shielding blocks, (2) earth berm surrounding an active disposal unit, and (3) remote operations with canes, camaras, etc.

As each disposal unit is completed, the concrete cover is installed. (Additional earth cover maybe added to reduce the surface radiation.) When an entire cluster is completed, the engineered cover is installed over the entire cluster. The concrete cylinder benchmarks denoting the location of disposal units are then installed.

At the end of commercial disposal operation, the facility's decontamination and decommissioning (D&D) is initiated. The remaining disposal units are closed after disposal of the facility's radioactive D&D waste. Other site closure activities includes: (a) partial dismantlement of the site perimeter berm, (b) D&D of retention ponds, and (c) installation of the final site cover.

STABILITY ANALYSIS

To assure long-term integrity of the EMCB disposal system, the engineered system was analyzed with respect to structural stability, slope stability and differential settlement. The analysis showed the designed system met all design criteria for stability.

Structural Stability

The EMCB is designed with structural stability to provide long-term isolation of the waste, to meet the performance objectives, and to avoid the need for active maintenance. Each component of the design provides additional, redundant stability that increases the overall margin of safety of the entire EMCB system. The EMCB design does not take credit for any additional waste form stability requirement than are currently practiced. Specifically, all Class B/C waste is stabilized to a minimum loading of 55 psi and no liquid waste is acceptable as required by 10 CFR 61.56.

The principal design criteria for the EMCB and the basis for their acceptance ensuring the long-term stability include: (a) the design loads; (b) load combination; (c) design codes, standards and regulatory guides; and (d) boundary conditions established from site characteristics.

The design loads for the EMCB disposal system consists of dead loads, live loads and earthquake loads. The typical dead load considered in the stability analysis includes the weight of the construction materials and the wastes. For design, the Class A waste is assumed to have an average unit weight of 80 pcf and solidified Class B/C wastes has 110 pcf. The live loads included 39 psf for snow loads, 250 psf for construction surcharge load, and 50 psf for wind loads (during construction). The earthquake load included a horizontal acceleration of 0.15 g and a vertical acceleration of 0.1 g.

The load combinations used for the design of EMCB system are in conformance with American Concrete Institute (ACI)-318 for Class A EMCBs, and ACI-349 for Class B/C EMCBs, as appropriate (6). The stability analysis of the EMCB included the detailed evaluation of the reinforced concrete retaining wall structure. Four loading conditions that the EMCB will experience in its service life follow.

1. When the below-grade portion of the disposal cell is fully filled and the retaining wall of the EMCB is subjected to the lateral loads resulting from the emplaced waste at one side and no backfill placement at the other side.

2. When the above-ground tumulus is completely constructed.

3. When the bunker experiences a construction surcharge load of 250 psf above an installed engineered cover.

4. Combining loading condition 3 with an earthquake loading.

The results from the stability analyses for these loading conditions, in terms of overturning, sliding and bearing stress, are presented in Table 1. The safety factors obtained from these stability analyses offer ample safety margin preventing any failure from overturning, sliding and bearing stress of the EMCB disposal structure.

Slope Stability

The stability of slopes were analyzed for possible impact on the operation, performance, and long-term stability of the EMCB disposal units. The excavated slopes were those created by the excavation of the below grade concrete bunkers, at a slope of 2 horizontal to 1 vertical for a depth of 12 ft. for Class A EMCB and 15 ft. for Class B/C EMCB. The permanent side slope of the earth mound consists of compacted clay abutting against the EMCB cluster and constructed to 5 horizontal to 1 vertical slope.

The slope stability analyses were performed using the conventional two dimensional slip circle and wedge methods. To assure short-term stability of the excavated slope, the minimum acceptable factor of safety was 1.2 for static loading condition. The safety factors of 2.5 and 2.3 were calculated for Class B/C EMCB excavated slopes, and 3.2 and 2.9 for Class A EMCB excavated slopes.

For long-term stability of permanent slopes, the minimum acceptable factors of safety were 1.5 and 1.1 for static and seismic loading conditions, respectively. The calculated safety factors were 2.8 and 3.4 for Class B/C EMCB permanent slopes and 2.7 and 3.3 for Class A EMCB permanent slopes from slip circle and wedge methods, respectively. Under the seismic condition, calculated minimum safety factors from the slip circle and wedge method were 1.8 and 2.1, respectively, for Class B/C EMCB permanent slopes, and 1.9 and 2.0 for Class A EMCB permanent slopes.

Settlement Considerations

Excessive differential settlements may adversely affect the performance or the long-term stability of the EMCB disposal system by (a) overstressing structural members, (b) affecting the engineered soil cover, and (c) damaging the underdrain system.

The design considerations and criteria were selected to accommodate the anticipated settlements caused by the consolidation of subsoils and included (a) using the partial load-compensated method for foundation design; (b) a uniform loading condition, and (c) limiting values for differential settlement not exceeding 0.004 L, where L is the distance measured from any two points within the EMCB.

A detailed settlement analysis was performed following the staged construction and waste emplacement sequence. The maximum total settlements at the center of a Class B/C bunker cluster (117 x 117 ft.) was estimated to be 6.6 in., with a 7 in. settlements at the ends of the cluster. The maximum differential settlement between the center and the ends of Class B/C EMCB was calculated to be less than 0.5 in., well within the design tolerance. The maximum total settlement at the center of a Class A bunker cluster (378 x 378 ft.) was estimated to be 8.34 in., with a 8.28 in. settlement at the ends of the cluster. The maximum differential settlement between the center and the ends of Class A EMCB was estimated less than 0.1 in., which is considered insignificant.

SAFETY ASSESSMENT

The safety assessment of the EMCB concept was performed to confirm that the design meets the requirements of 10 CFR Part 61, NUREG-1199(5) and NUREG-1200(7).

Waste Characterization

The source term for the safety assessment was obtained from NUREG/CR-4370(8). The project specified that the disposal facility be located in the northeastern United States and receive 7,080 cubic meters (250,000 cubic feet) of waste per year for 30 years. The 30-year operating life of the facility was divided into two distinct periods. During the first 25 years of operation, the disposal facility would receive LLW from the normal operation of the nuclear power plants and from institutional and industrial facilities. Based on DOE/LLW-59T (9), 60% of the volume of waste was received from nuclear plants and 40% from institutional and industrial facilities. This waste was assumed to be composed of 80 individual normal operation waste streams described in NUREG/CR-4370 (8). A constant radionuclide composition was assumed for the initial 25 years of operation.

For the final five years of operation, the disposal facility was assumed to receive waste from the decommissioning of nuclear power plants only. This assumption implies that a second LLW disposal facility is available to receive the normal operation waste being generated during this time period. As with the normal operation waste, NUREG/CR-4370 was used to determine the characteristics of the decommissioning wastes received, including both PWR and BWR decommissioning waste streams.

Recent studies have shown that "traditional" values of the concentration of some radionuclides in LLW, particularly iodine-129, have been greatly overestimated. Reference 10 demonstrated that the "traditional" I-129 LLW concentration is at least an order of magnitude, above the actual concentration. The reason may be that when I-129 concentration measurements were made and no I-129 was detected, the instrument's minimum detectable concentration was reported as the actual I-129 concentration in the waste. However, the safety assessment of the EMCB did not take advantage of this recent development to reduce the NUREG/CR-4370 I-129 concentrations.

Groundwater Dose Model

IMPACTS, a computer code (8) was used for the safety analysis. The computer code assumes a simple groundwater transport model for radionuclide migration to calculate public dose. This model assumes water enters the disposal facility and leaches the radionuclides from the waste. The dissolved radionuclides then migrate vertically through the unsaturated zone to the water table, which is the upper boundary of the saturated zone. Finally, the radionuclides migrate horizontally through the saturated zone to a dose receptor point. It should be noted that the groundwater dose analysis was not used to optimize the design of the EMCB. Rather, the dose analysis was used to verify that the design developed from good engineering principles could meet the requirements of 10 CFR Part 61.

The groundwater model was based upon the following site geological parameters.

<u>Site Geology</u>

Strata	Thickness (meters)	Permeability (cm/sec)
Recent Alluvium	.3 - .6	-
Glacio-fluvial Soil	6.1	10^{-5}
Lacustrine Clay	19.8	10^{-8}
Weathered Rock	0.9	10^{-7}
Shale	30.5	10^{-8}
Silty Sandstone	30.5	10^{-5}

The high permeability of the glacio-fluvial layer results in a seasonal flow of water, or a perched aquifer. Because of its shallow depth (20 feet) and intermittent nature, this aquifer cannot yield sufficient water for a well. However, it may enable radionuclides seeping out of the facility to reach a nearby stream. Another pathway by which the radionuclides could enter the drinking water is via the deep aquifer beneath the water table, which lies within the shale layer, at a depth of 27.4 meters (90 feet). Due to its low hydralic conductivity, this layer would be a poor aquifer. Nevertheless, it was conservatively assumed to supply water to a well used by a single family. The safety assessment includes the calculation of doses due to the consumption of water from such a well and also from the nearby stream.

The EMCB is provided with an engineered cover consisting of layers of soil, sand, gravel, clay, high density polyethylene (HDPE) and concrete. The rate of infiltration of water into the bunker was simply calculated according to Darcy's Law, which stated that the infiltration rate is equal to the hydrostatic pressure or hydraulic head divided by the effective resistance. Since the cover was specifically designed to prevent water from accumulating above the clay layer, it was assumed that the clay layer was saturated with water and water pooled above the HDPE layer. No credit was taken for the concrete to resist water infiltration or exfiltration.

After the 100-year institutional care period of the EMCB, two adjustments were made to the infiltration model. First, credit for the HDPE layer was no longer taken. Second, consistent with NUREG/CR-4370, it was assumed that ten percent of the engineered cover will be disturbed and replaced with natural cover that has a higher hydraulic conductivity.

Although IMPACTS allows doses to be determined up to 5000 years into the future, the time period of the EMCB safety assessment was limited to 1500 years after closure. The basis was the reference to U.S. EPA Health and Environmental Protection Standard for Uranium and Thorium Mill Tailings (40 CFR 192.02(a)), which states "control shall be designed to be effective for up to one thousand years, to the extent reasonably achievable, and, in any case, for at least 200 years..." The 1500 years applied for this analysis represents 1000 years beyond the 500 year intruder barrier requirement of 10 CFR 61.52 (a)(2).

The results show that the doses from the EMCB via the groundwater pathway are well within the limits of 10 CFR 61.41. The radioactively-contaminated plume does not reach the deep aquifer well within the 1500-year cutoff time of our analysis. The dose to the thyroid of the maximum exposed individual from drinking water contaminated by the perched aquifer is 2.5 millirem per year. All other organ doses were determined to be below 0.1 millirem per year. These maximum doses were calculated to occur at the 1500 year cutoff time. The peak dose occurred after the 1500 year cutoff.

Normal Operation Dose Models

Under normal facility operation radioactive releases from the facility are not expected to occur. Nonetheless, a bounding normal operation source term was devised to that conservative off-site doses could be calculated. Each of the waste containers received at the EMCB was assumed to have its total surface area contaminated to the maximum extent allowed by 10 CFR 71.87, Table V (i.e., 10^{-5} uCi/cm^2). Again, this bounding assumption is not considered credible, but it gives a simple, conservative means of determining normal operation releases. In order to arrive at a radionuclide breakdown, it was assumed that the surface contamination had the same average composition of radionuclides as the waste within the containers. Then, all of this radioactive contamination was released to both the atmosphere and in the liquid discharge. This double accounting of the surface contamination meant that the resultant airborne pathway doses should not be added to the liquid pathway doses.

It should be noted that the EMCB is provided with a liquid collection system that drains and collects any water from the bunkers in a retention pond where it can be sampled, and, if necessary, processed to reduce its radioactivity. This will ensure that all liquid radioactive releases are controlled and are below the 10 CFR Part 20 maximum permissible concentrations.

For the airborne releases, two sources were assumed. One percent of the total annual amount of carbon-14 received at the EMCB was assumed released to the atmosphere. Also included in the airborne source term was radon-222 generated from the decay of radium-226. All radon-222 generated in the open bunker was assumed to be released.

Meteorological and surface water data from the same, hypothetical northeastern site used for the groundwater model was utilized in this analysis. The dose methodology presented in Regulatory Guide 1.109 (11), as implemented in the GASPAR and LADTAP computer programs, was used to determine the normal operation doses. Doses from all pathways, except food irrigation, were determined. All doses to the maximum exposed individual are well below the limits of 10 CFR 61.41. Carbon-14 was found to be the dominant contributor to the ingestion and inhalation dose pathways, while cobalt-60 was found to dominate the shine dose pathways.

The EMCB has several design features which are intended to help reduce shine dose exposures to as low as is reasonably achievable (ALARA). These include segregating lower activity waste to act as a shield for higher activity waste as it is placed in the bunkers. Also, earthen berms are provided around the periphery of the bunker to act as shadow shields. Finally, the Temporary Waste Storage Building (TWSB) is provided in order to reduce the shine dose from uncovered waste in the Class B/C bunkers. With these features, the maximum shine dose at the site boundary from (1) the uncovered waste in the active disposal bunkers, (2) the TWSB, and (3) waste in transit on site, was determined to be approximately 8 millirem per year. The shine dose rate was determined using standard industry shielding codes DOT and ISOSHLD. Cobalt-60 was found to be the major contributor to the off-site shine dose.

The EMCB was designed with a bio-intrusion barrier to prevent radionuclide transport by plants and animals and, therefore, the doses from this pathway were reported to be nonexistent.

Accident Analysis

Consistent with the recommendations of NUREG-1199 and 1200, Ebasco analyzed the two limiting accident scenarios. For the EMCB, these scenarios are a fire in an open bunker and the dropping of a waste liner into an open bunker. The IMPACTS program was used to determine the amount of radioactivity that becomes airborne either during a fire or as the result of a dropped liner. Worst case methodology (i.e., stability class F and a wind speed of 1 meter per second), instead of actual site meteorology, was entered into IMPACTS for the accident analysis.

In 10 CFR Part 61 there are no regulatory limits on the allowable doses following a design basis accident at a LLW disposal facility, comparable to the 10 CFR Part 100 limits for nuclear power plants. It was decided to use the 500 millirem whole body unrestricted area annual dose limit from 10 CFR 20.105 as the EMCB accident dose limit.

The results of the analysis show that a fire in an open bunker is the worst case accident at the EMCB. The off-site dose to each organ of the maximum exposed individual due to such a fire is below 500 millirems, except for the bone dose which is less than 900 millirems. However, considering that the ICRP (12) whole body equivalent weighting factor for bone is .03, the bone dose is considered acceptable.

COST ESTIMATE

The life cycle cost of this disposal facility is shown on Table 2. The estimates are in 1988 dollars. The annual operations cost includes a levelized annual construction cost for the EMCB structure. This cost estimate for EMCB disposal is comparable with the cost of other engineered disposal alternatives.

CONCLUSIONS

The above safety assessment and stability analysis show that the EMCB technology is a viable option for meeting the Performance Objectives of 10 CFR Part 61. The above design incorporates many redundant design features and large design margins to assure long-term integrity.

It should be recognized that the above analyses employed simplified analytical techniques due to the limited resources available and the demonstration purpose of this project. More sophisticated analytical techniques would be warranted for real case evaluation.

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TABLE 1: SUMMARY OF STABILITY ANALYSES

CLASS A EMCB

Loading Condition	Factors of Safety		Bearing Stresses (ksf)		
	Overturning	Sliding	Toe	Heel	Allowable
1	5.2	5.6	1.20	1.0	3.15
2	2.4	N/A	2.68	0.6	4.27
3	2.64	N/A	3.20	4.10	16.37
4	1.86	N/A	4.20	4.10	5.47

CLASS B/C EMCB

Loading Condition	Factors of Safety		Bearing Stresses (ksf)		
	Overturning	Sliding	Toe	Heel	Allowable
1	2.37	3.37	3.64	0.39	3.71
2	2.96	47.7	3.25	2.0	4.90
3	2.03	N/A	4.15	3.57	17.94
4	1.43	N/A	6.63	2.95	8.55

Note: The minimum acceptable factors of safety for loading condition 1 through 3 is 1.5, and 1.1 for loading condition 4.

TABLE 2

COST ESTIMATE EMCB DISPOSAL FACILITY

DEVELOPMENT (6 year total)	Total $30,100,000
a. land	700,000
b. Licensing	10,800,000
c. Property Development	7,100,000
d. Buildings	8,200,000
e. Equipment	3,300,000
OPERATIONS (Annual)	Total $ 7,300,000
a. Salaries	2,700,000
b. Bunker Cluster Construction	
Class A	1,100,000
Class B/C	400,000
c. Administrative and Utility	400,000
d. Maintenance Expenses	1,100,000
e. Interest Expenses (1st year)	1,600,000
f. Operator's Fee (and taxes)	- Not Included -
CLOSURE AND SURVEILLANCE (5 year total)	Total $ 8,000,000
LONG-TERM INSTITUTIONAL CARE (Annual)	Total $ 200,000

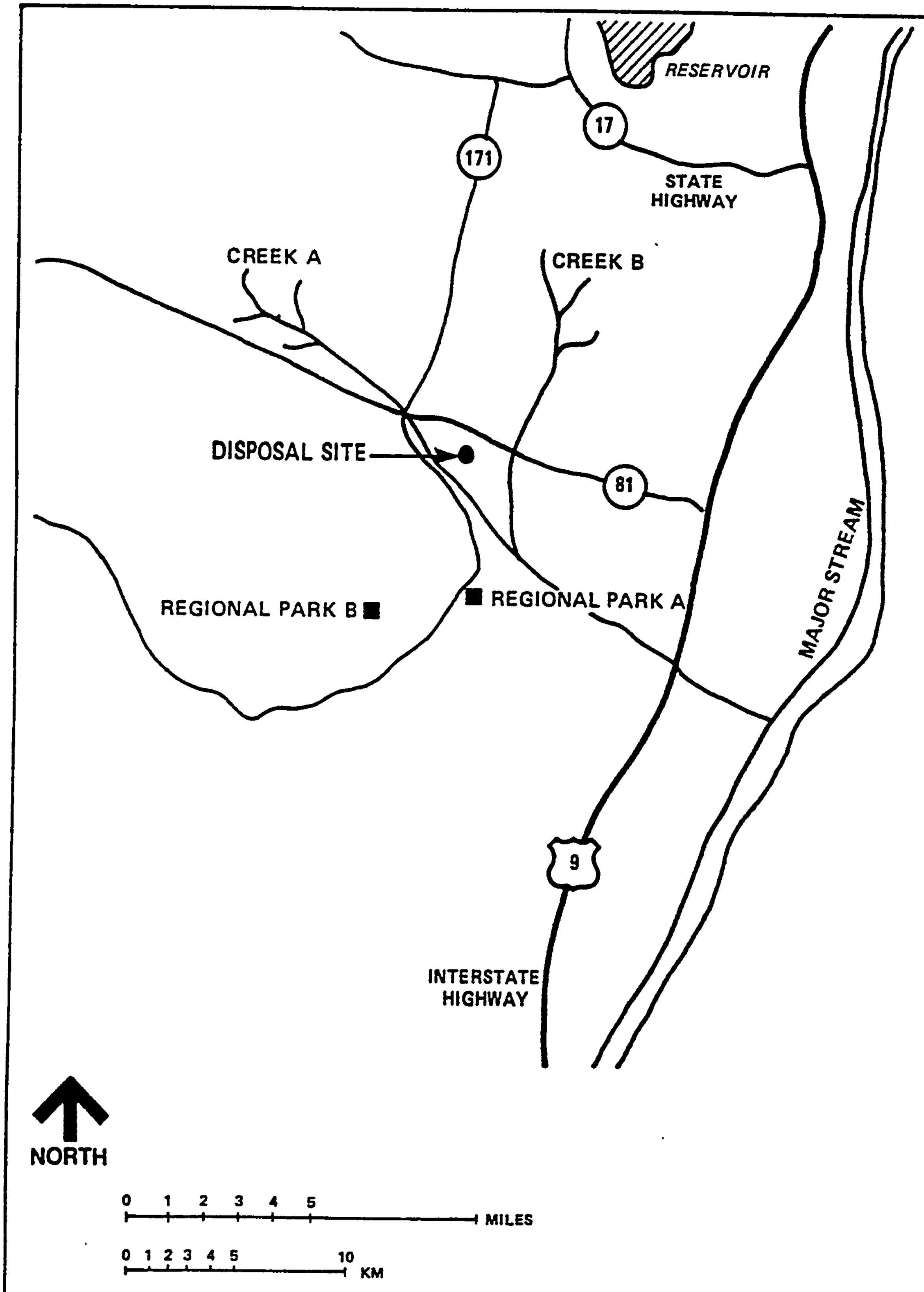


FIGURE 1

REGIONAL SITE LOCATION MAP

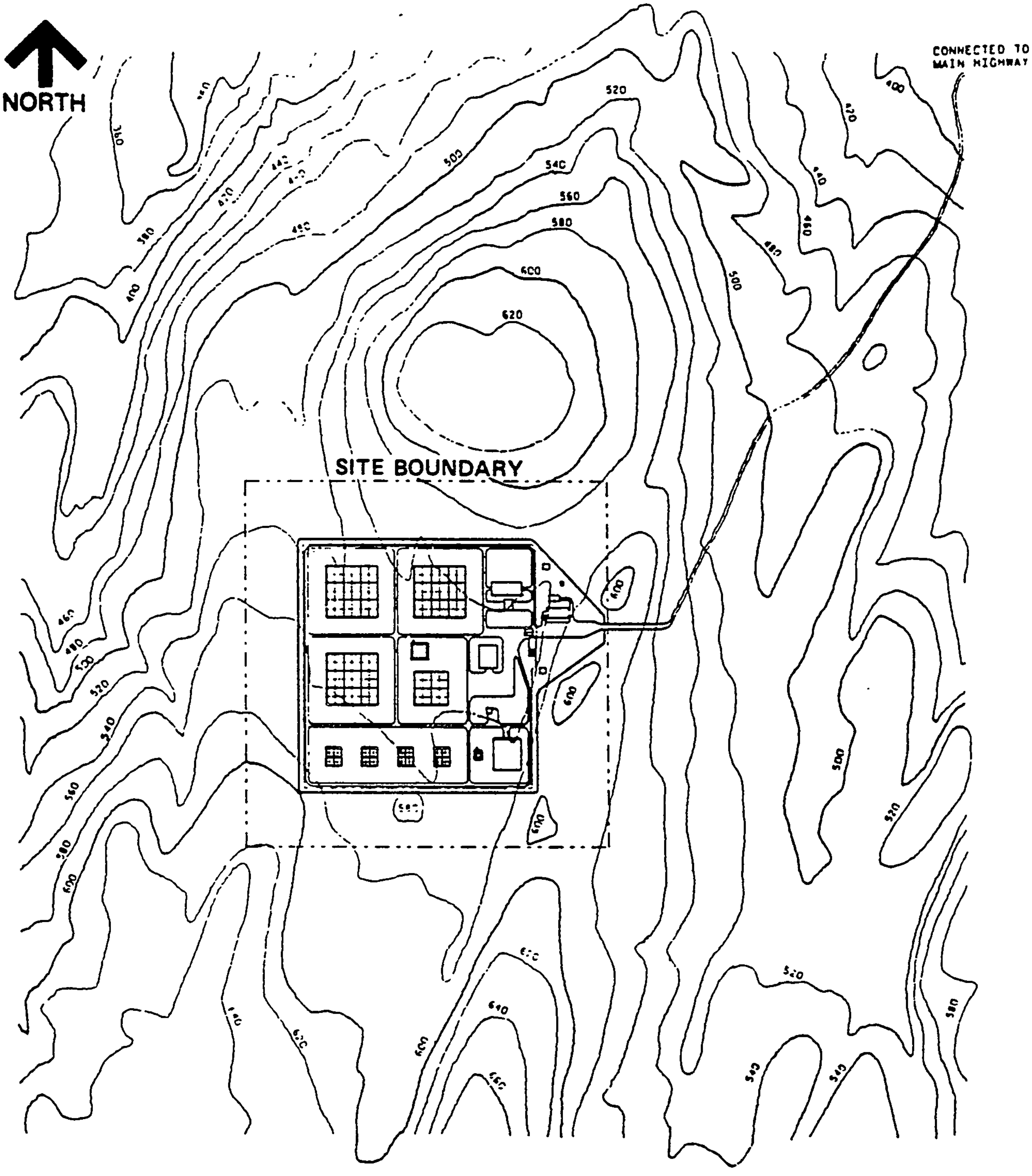


FIGURE 2

SITE PLAN

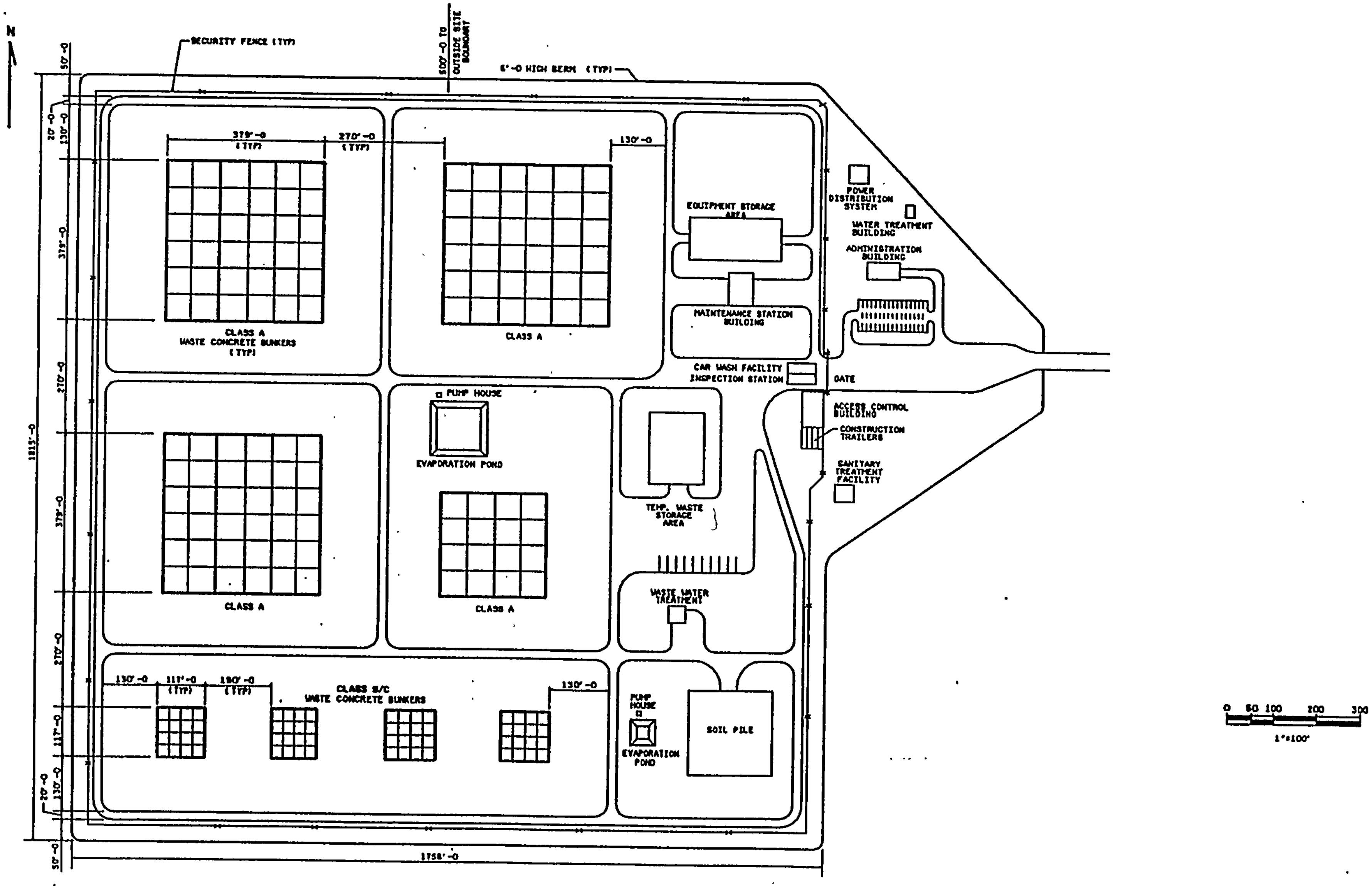
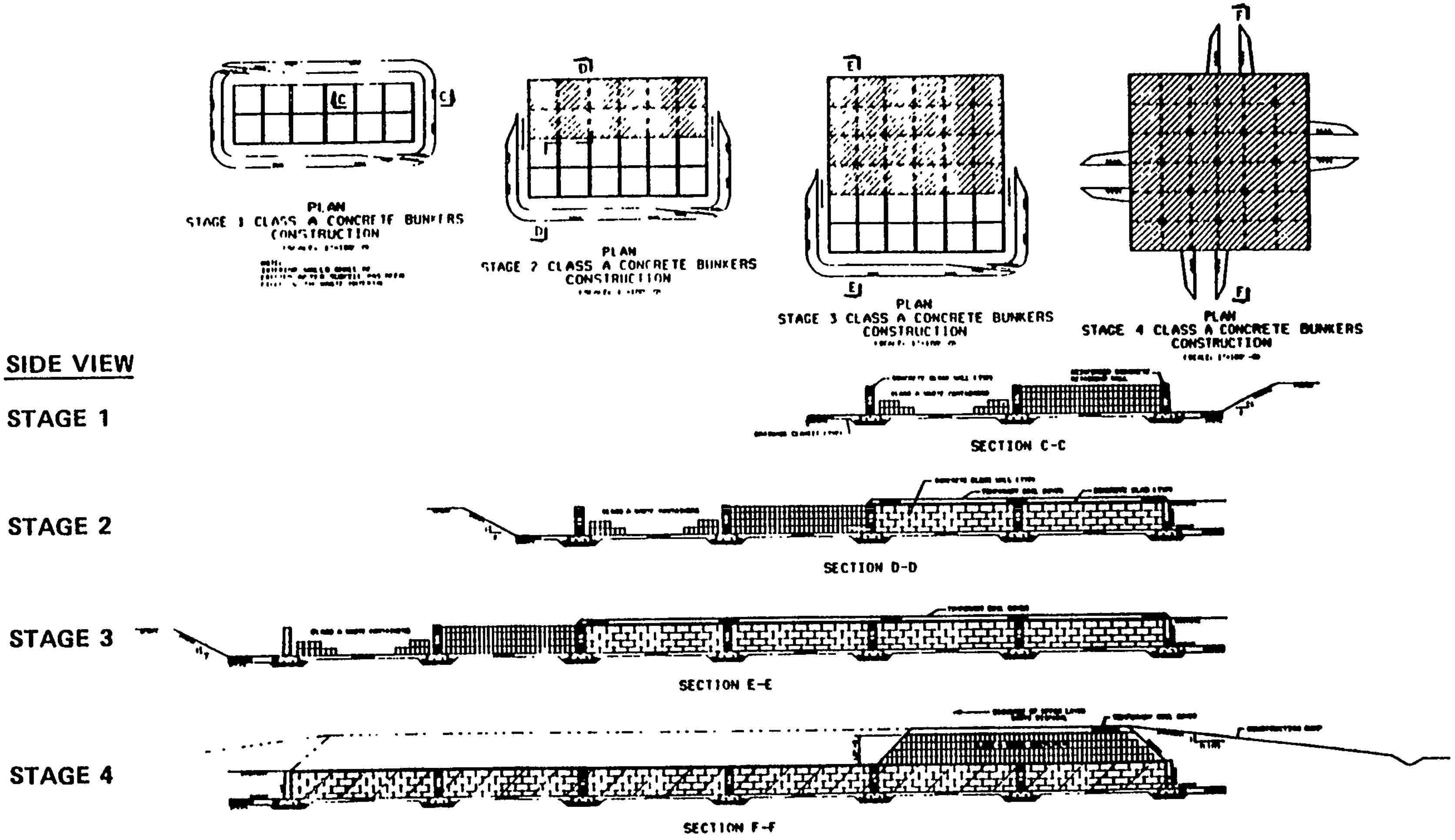


FIGURE 3: DISPOSAL FACILITY SITE PLAN



NOTE: NOT TO SCALE

FIGURE 4

DEVELOPMENT OF CLASS A EMCB

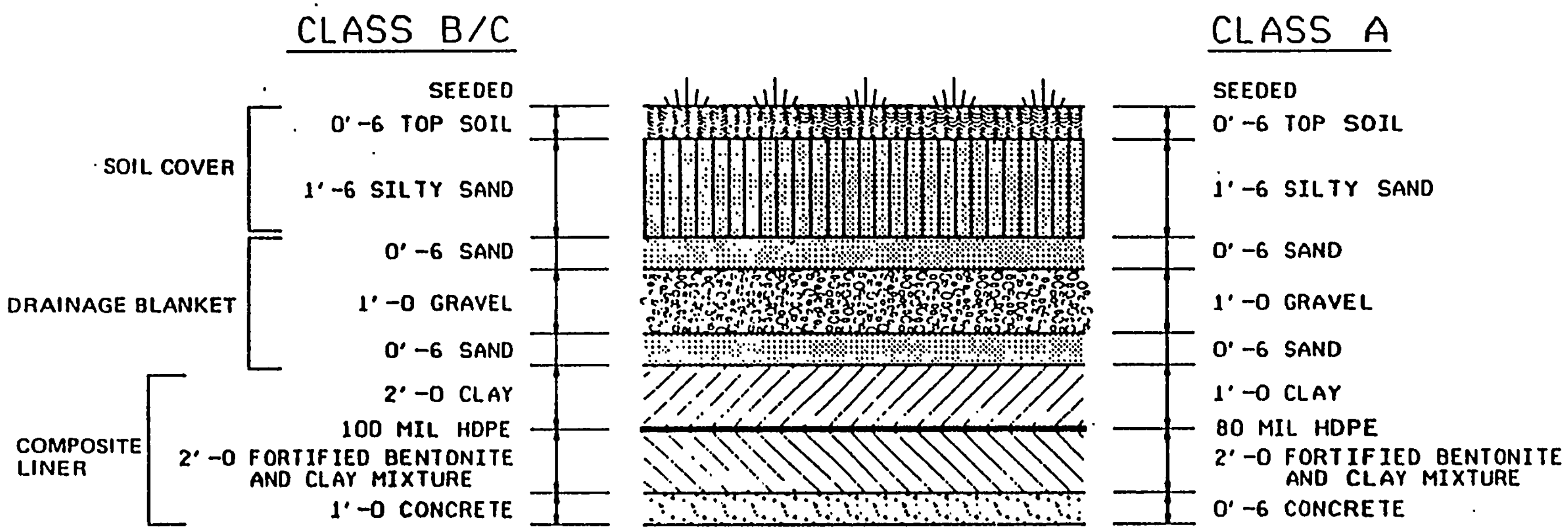


FIGURE 6: MULTI-LAYER ENGINEERED COVER

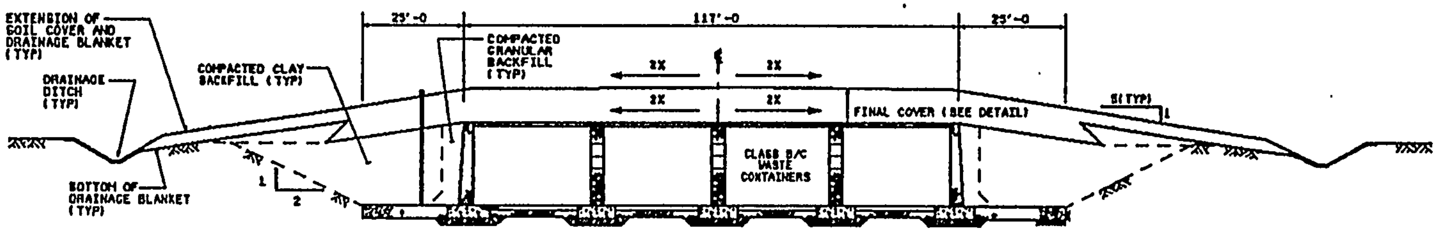


FIGURE 5: CROSS-SECTION OF CLASS B/C EMCB

Overview of NRC Review Process

by

Michael Tokar and Joseph D. Kane

ABSTRACT

This paper describes the NRC staff's review of the Prototype License Application Safety Analysis Report (PLASAR) for an Earth-Mounded Concrete Bunker low-level waste disposal facility. Described are the objectives of the review, the resources (e.g., background guidance documents and staff technical disciplines) used, and the products produced. Evaluation conclusions are summarized.

INTRODUCTION

The Low-Level Radioactive Waste Policy Amendments Act (LLRWPAA) of 1985 requires the U.S. Nuclear Regulatory Commission (NRC) to identify methods for the disposal of low-level radioactive waste other than shallow-land burial, to establish and publish relevant technical information regarding those alternative methods, and to publish technical requirements that such alternative facilities should meet if pursued as a substitute for shallow land burial. The NRC met the requirements of the LLRWPAA related to alternative methods of disposal through the publication of various guidance documents, including several technical papers, Branch Technical Positions, NUREG reports (NUREG-1241, NUREG/CR-3774, and NUREG/CR-5041, NUREG/CR-5054), and a Standard Format and Content Guide (NUREG-1199, Rev. 1) and Standard Review Plan (NUREG-1200, Rev. 1). In addition, in response to requests by the States for more licensing and technical guidance on engineered alternatives, the NRC agreed to perform a "mock licensing review" of two soil-covered options considered by the NRC to be most viable from a licensing standpoint: (1) the earth-mounded concrete bunker (EMCB); (2) the below-ground vault (BGV). This summary addresses the NRC staff's technical review of a Prototype License Application Safety Analysis Report (PLASAR), which was prepared for the Department of Energy (DOE), under the Department's Technical Assistance Program (established in response to the LLRWPAA) to States and compact regions. The EMCB PLASAR was prepared by Ebasco Services Incorporated (EBASCO) under contract to EG&G Idaho, Inc., DOE's lead contractor for its Low-Level Waste Management Program.

The NRC has focussed its attention and guidance on soil-covered options such as the EMCB and BGV because of the realization that engineered structures for low-level radioactive waste disposal would have an expected minimum period of performance of 300 to 500 years. It is anticipated that such structures will be largely constructed of Portland cement concrete, which from a long-term materials durability standpoint requires protection from the potentially deleterious effects of various climatological phenomena such as freeze/thaw cycles and acid rain. Thus, the earthern cover to be placed over the concrete structure would provide protection for the concrete from potentially adverse climatological effects and would also provide an additional barrier to radiological release and inadvertent intruders. The EMCB disposal concept benefits also from the fact that there is design and operational experience available from France, where the EMCB is the engineered disposal method in use at the Centre de la Manche facility. Moreover, as noted in the EMCB PLASAR, the EMCB disposal technology also has the advantage of having the capability of being employed on a site with a relatively shallow groundwater table because the facility would be partially above-grade. The NRC's regulation for land disposal of low-level radioactive waste, 10 CFR Part 61, indicates that contact of waste by water should be minimized so as to minimize the potential for release of radionuclides by leaching form the waste form. Thus, because there are restrictions in Part 61 against allowing disposal below or in the zone of fluctuation of the water table, an EMCB could conceivably be placed on a site that might be incompatible with some totally below-grade facilities.

REVIEW PROCESS

Review Objective

The primary objective of the EMCB PLASAR review was to provide assistance to the States and regional compacts by (a) identifying acceptable and unacceptable alternative design features and concepts and (b) demonstrating, by example, how to use the NRC's Standard Review Plan (NUREG-1200). In addition, it was recognized that the mock licensing review would provide the NRC staff with valuable practical experience in using the Standard Review Plan (SRP) in conducting a low-level radioactive waste facility licensing review.

And, the review would also allow weaknesses in the SRP (and licensing process) to be identified so that improvements might be made. Because the emphasis of this mock licensing review was focussed from the start on the need to provide assistance concerning the specific technological aspects of engineered alternative methods of disposal, not near-surface disposal in general, the review concentrated on the design and operations-related portions of the PLASAR. Specifically, resources were mainly focussed on PLASAR Sections 3) DESIGN AND CONSTRUCTION and 4) FACILITY OPERATIONS, both of which received a detailed review. To a somewhat lesser extent, significant attention was also devoted to Sections 5), SITE CLOSURE PLAN AND INSTITUTIONAL CONTROLS, 6) SAFETY ASSESSMENT, and 7) OCCUPATIONAL RADIATION PROTECTION. However, other PLASAR sections, such as Section 2, SITE CHARACTERISTICS, which contains primarily hypothetical information, were addressed only minimally; for example, Section 2 was examined in a cursory way within the context of whether the assumed site conditions might adversely affect the performance of the EMCB. The site information was not reviewed from the standpoint of determining the adequacy of the information presented, the quality of the data, or the ability of the discussion to meet the acceptance criteria in the Standard Review Plan and Part 61. Sections 8) CONDUCT OF OPERATIONS and 10) FINANCIAL ASSURANCE were not reviewed because applicant-specific information on these topics was not germane to a prototype safety analysis report. On the other hand, though little information was provided on PLASAR Section 9 on QUALITY ASSURANCE, this section was reviewed in some detail by the NRC staff, and comments and questions were developed because of the recognized importance of the subject.

Resources

In reviewing the EMCB PLASAR, the technical reviewers relied extensively on Revision 1 of the Standard Review Plan (NUREG-1200) and certain background documents such as Volume 2 of NUREG/CR-5041 (on recommendations for review criteria for EMCBs), NUREG/CR-5054 (on recommendations for review criteria on environmental monitoring and surveillance programs) and NUREG-1293 (on quality assurance guidance for low-level waste facilities). The review team consisted primarily of staff from the Division of Low-Level Waste Management and Decommissioning (DLLWM) in NRC's Office of Nuclear Materials Safety and

Safeguards (NMSS). The review effort was assisted in specialized technical areas by private consultants and staff from the U.S. Army Corps of Engineers (COE) and Brookhaven National Laboratory (BNL). Technical disciplines involved in the review effort included groundwater hydrogeologists and surface water hydrologists, geotechnical engineers, structural engineers, civil engineers, materials engineers, seismologists, health physicists, quality assurance specialists, performance assessment specialists, and a licensing project manager. Approximately 3100 hours (equivalent to about 2-person years) of effort were expended in the review by DLLWM staff, while another half-person year of work was conducted by contractor staff. It should be noted that, because of the fictitious nature of the "mock" review, certain activities that would normally be undertaken as part of the review process were omitted. For example, no independent audit calculations or site visits were conducted, and no examinations were made of data collection methods. Considering the fact that (1) these numbers reflect only a partial first-round review of only some of the technical areas that would be reviewed in an actual licensing review for a real facility, and (2) the review was conducted by experienced personnel with many years of technical and regulatory experience, it can be anticipated that significantly more effort would be required to conduct a full and comprehensive review of an actual application, especially if inexperienced technical staff were used.

Guidance Documents

In performing the review, the primary reference guidance document used was Revision 1 of the Standard Review Plan (SRP), which was issued in January 1988. Both Revision 0 (issued in January 1987) and Revision 1 of the SRP address near-surface disposal of low-level radioactive waste. However, Revision 0 was directed primarily toward trench-type disposal, whereas Revision 1 incorporates additional sections and information dealing with alternative disposal methods such as belowground vaults and earth-mounded concrete bunkers. The importance of the SRP in the conduct of the review cannot be overemphasized. The SRP establishes the areas of review (i.e., the information reviewed) in each section of the licensing document, the procedures used in the review, and (very importantly) the acceptance criteria used in the review. Inasmuch as several of the review team members had had no prior involvement with the SRP before the PLASAR review, this effort provided invaluable experience to the staff and enabled an identification to be made of areas for further improvement in the SRP and related guidance documents such as Technical Positions. The experience obtained in conducting the technical review indicated that significant improvements could be made in several technical areas if additional guidance were available. Thus, if additional guidance could be provided, there would be further assurance that license applications could meet the 15 months review schedule.

Review Products

The technical review conducted on the EMCB PLASAR can best be characterized as a modified "first-round" review. An actual review of a real license application for a low-level radioactive waste disposal facility is expected to be an interative process involving two or more formal "requests for further information" (i.e., 1st-round, 2nd-round, etc. questions) together with unspecified informal interactions between the NRC staff and applicant in the form of meetings and telecommunications. In the EMCB PLASAR review, only one round of questions and comments was prepared, and, as described earlier, not all of the areas that would be evaluated in an actual license application were reviewed. Moreover, while in an real licensing review there would be various interfacing opportunities for the staff and applicant to obtain clarification on issues, that practice was not followed in the EMCB PLASAR review because of constraints on staff resources that proscribed such interactions. As a result, some of the questions and comments included in this report on the PLASAR review would not exist in a real licensing review (because the needed clarifications would have been obtained informally). In addition, several questions and comments concerning missing information in the PLASAR were included even though the information was (presumably intentionally) omitted from the PLASAR by EBASCO due to their contractual agreement with DOE that certain areas of information would not be included in the prototype report. This category of questions and comments was included to enable potential future applicants and State and regional compact regulators to know the extent of information that would be expected to be provided in a real application.

The comments and questions generated by the EMCB PLASAR review team addressed perceived deficiencies in the SAR document. There was, however, much good information in the document that was consistent with the requirements of Part 61 and the recommendations in the Standard Review Plan and other NRC guidance documents. Therefore, to provide a clearer and more balanced description of the technical review, a summary report was prepared. This summary report, or "Safety Evaluation Status Report," (SESR), follows to the extent practicable the format and content of an actual final Safety Evaluation Report (SER) that would be developed for a real application review. For each selected review area and corresponding SRP section, the SESR describes the adequate and inadequate aspects of the information provided in the PLASAR and the basis for the staff's conclusions. However, because (1) the review did not proceed beyond the equivalent of a first-round of questions, and (2) certain technical areas received little or no review, it was not appropriate to develop formal regulatory "findings" that certified that particular sections of Part 61 or other NRC regulations were satisfied. Moreover, because staff resources were required to adapt to changing regulatory issues and prioritization of licensing work, it was not possible to address all the review areas in the SESR. In technical areas affected by such resource limitations, questions and comments were provided without the corresponding SESR input. The sections that were completed in the SESR are considered by the NRC staff to be good examples of the safety assessments that are necessary as part of a licensing review to support the technical basis for regulatory acceptance or rejection and which can be defended before a licensing review board.

EVALUATION CONCLUSIONS

In their analysis of the EMCB disposal facility, DOE's contractors, EG&G and EBASCO, attempted to follow the guidance in the two principal NRC guidance documents (the SRPs and the SF&C) on LLW disposal. The degree of success attained in following the NRC guidance documents, and in fulfilling the regulatory requirements of 10 CFR Part 61, varied widely, however. Some information in the PLASAR sections is clear, comprehensive, and is a direct response to the requests in the regulatory guidance documents. Other sections provide very little information, and often are only a repetition of the information recommendations in the guidance documents themselves.

For example, with the exception of surface drainage and erosion protection considerations, the information described for the principal design features in PLASAR Section 3.1 is generally acceptable. In PLASAR Sections 3.2 and 3.3, the information provided for the structural design and construction considerations for the EMCBs is clear and comprehensive; however, several staff review comments and questions were developed because the PLASAR did not provide supporting analyses and documentation for deviations from the NRC guidance documents. Review comment number 17 is an example that addresses the staff concern about the PLASAR's lack of a supporting basis for deviating from the recommended impervious foundation design. The large number of review comments and questions on PLASAR topics that include infiltration, surface and subsurface drainage, radiation protection, environmental monitoring, and subsidence and settlement in Section 3.2 of the PLASAR is a reflection of significant deficiencies in the information that was provided in these areas. These same topics are not adequately addressed in other related PLASAR sections, where it was expected that more detailed design information would be provided. The discussions on the design of auxiliary systems and facilities in PLASAR Section 3.4 are generally not adequate, because of insufficient information that would permit an assessment of any adverse effects on the design and safe operation of the LLW disposal facility due to the malfunctioning or failure of the auxiliary systems.

In Section 4.0 of the EMCB PLASAR, the staff evaluation of the information provided on receipt and inspection of waste, waste handling and interim storage, and on waste disposal operations indicated that, overall, the information is only partially complete. A major theme that extends throughout the staff's review comments is the need for the PLASAR to provide specific operational procedures for the topics in Section 4.0. The information provided in Section 4.4 of the PLASAR on operational environmental monitoring and surveillance, is considered to have major deficiencies, which later adversely impact the intended continuation phase in postoperational environmental monitoring in Section 5.3.

The information provided in EMCB PLASAR Section 5.0 continues to reflect significant deficiencies in the discussions on drainage and erosion protection. Several of the staff's review comments are directed at improving the PLASAR's coverage on structural performance monitoring, particularly the aspects related to the duration of monitoring, the establishment of allowable monitoring limits and to specific information on installation details. Information on Section 5.2 of the PLASAR on decontamination and decommissioning (D&D) was purposely limited, because it was felt a detailed D&D plan was outside the scope of the PLASAR study.

The information provided in the PLASAR sections on Safety Assessment (Section 6.0) is considered to be insufficient, as evident by the large number of review comments and questions in these areas. Because of limited staff resources, SESR input on safety assessment topics in the EMCB PLASAR was not prepared at this time in the mock review.

The information provided on occupational radiation protection in Section 7.0 of the PLASAR is considered to be significantly deficient, and in need of major reorganization. SESR input on Section 7.0 by the NRC staff may also be available by August 1989, depending on the availability of resources.

The quality assurance information provided in Section 9.0 of the EMCB PLASAR is not sufficient and is essentially a restatement of the information recommendations defined in NUREG-1199. The PLASAR in Section 9.0 acknowledges that a full scope quality assurance plan was beyond the scope of the PLASAR effort.

An examination of the NRC staff review comments and questions on the PLASAR would indicate a common pattern in their development. Typically, the organization of the comment will include (1) a general statement on the review issue, (2) identification of the specific PLASAR concern or problem, and (3) a statement on what could be done to resolve the review issue.

The SESR input examples that have been provided illustrate the approach that is used by the NRC staff to perform a safety evaluation. Typically, in the individual SESR sections the format includes the following: (1) a summary description of the information provided in the PLASAR that is being addressed; (2) identification of the regulatory guidance used in the staff assessment and a statement on the review objective; (3) a description of the evaluation criteria used to assess the acceptability of the PLASAR information and the staff conclusion on acceptance; (4) suggestions for providing specific information in cases where the PLASAR information is considered incomplete; and (5) cross-referencing to the specific first-round comment that is pertinent to the missing information. Responsible branches and personnel that prepared the SESR input are listed in the SESR.

It is important to recognize the importance of an SER and the difficulties involved in completing a good one. The SER's importance stems from the fact that it serves as a complete and defensible summary of the regulatory review effort. In that regard, the SER is often used to support decisions in licensing hearings. The SER is the "bottom-line" document that records the regulatory staff decisions on safety and licensing acceptance. It must present a logical approach that will be defensible before the public, technical peers, and possibly a licensing hearing board. For these reasons the NRC staff has persevered as part of the review of the PLASAR in completing a sufficient number of SESR sections that can be of assistance to Agreement States and regional compacts. The staff has in turn benefitted from this SESR effort by gaining good, practical licensing review experience. Important lessons learned from NRC's participation in the PLASAR review include (1) recognition that large expenditures in staff resources are needed both to develop a working knowledge and experience with the regulatory guidance documents and the important referenced reports, and (2) that there is a need to establish a staff encompassing many scientific and engineering disciplines that can be dedicated to license application review, without delays and competition with other regulatory assigned duties, to meet a 15-month licensing review schedule.

SUMMARY

To provide assistance to States and regional compacts interested in licensing alternative methods of disposal of disposal of low-level radioactive wastes, the NRC staff performed a "mock review" of a Prototype License Application Safety Analysis Report for an Earth-Mounded Concrete Bunker low-level waste disposal facility. The mock review was intended to provide licensing guidance by (1) identifying acceptable and unacceptable design features and concepts and (2) demonstrating, by example, how to conduct a review using the NRC's Standard Review Plan. The review focussed primarily on the design, construction, and operations portions of the PLASAR. Considerable attention was also devoted to areas dealing with site closure, safety assessment, and occupational radiation protection. Information on siting was addressed only minimally.

The technical review conducted on the EMCB PLASAR was roughly equivalent to a "first-round" review of a license applicant's safety analysis report. Products resulting from the review consist of a set of questions and comments and a "Safety Evaluation Status Report" that address specific areas of review identified in the Standard Review Plan. The questions and comments focus on perceived deficiencies in the PLASAR's treatment of the technical areas of concern, while the SESR attempts to present a balanced description of the adequate as well as inadequate aspects of the information presented in the PLASAR. In general, while there was much good information in the PLASAR, the degree of success attained in following NRC guidance in fulfilling the requirements of Part 61 varied with the technical area discussed. Details are provided in the staff comments and questions and the SESR.