DOE/EM-0226

DEPARTMENT OF ENERGY
UNITED STATES OF AMERICA

Office of Environmental Management

Office of Technology Development

Chicago Operations Office

Technology Summary

MASTER

December 1994

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CHICAGO OPERATIONS OFFICE

TECHNOLOGY SUMMARY

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Foreword

This document has been prepared by the Department of Energy's (DOE) Environmental Management (EM) Office of Technology Development (OTD) to highlight its research, development, demonstration, testing, and evaluation (RDDT&E) activities funded through the Chicago Operations Office. Technologies and processes described have the potential to enhance DOE's cleanup and waste management efforts, as well as improve U.S. industry's competitiveness in global environmental markets. The information has been assembled from recently produced OTD documents which highlight technology development activities within each of the OTD program elements. These Technology Summaries (as well as other OTD documents) can be obtained through the EM Central Point-of-Contact at 1-800-845-2096 and include the following:

VOCs in Non-Arid Soils Integrated Demonstration, February 1994 - DOE/EM-0135P
VOCs in Arid Soils Integrated Demonstration, February 1994 - DOE/EM-0136P
Mixed Waste Landfill Integrated Demonstration, February 1994 - DOE/EM-0128P
Uranium in Soils Integrated Demonstration, February 1994 - DOE/EM-0148P
Characterization, Monitoring, and Sensor Technology Integrated Program, February 1994 - DOE/EM-0156T
In Situ Remediation Integrated Program, February 1994 - DOE/EM-0134P
Buried Waste Integrated Demonstration, February 1994 - DOE/EM-0149P
Underground Storage Tank Integrated Demonstration, February 1994 - DOE/EM-0122P
Efficient Separations and Processing Integrated Program, February 1994 - DOE/EM-0126P
Mixed Waste Integrated Program, February 1994 - DOE/EM-0125P
Rocky Flats Compliance Program, February 1994 - DOE/EM-0123P
Pollution Prevention Program, February 1994 - DOE/EM-0137P
Innovative Investment Area, March 1994 - DOE/EM-0146P
Robotics Technology Development Program, February 1994 - DOE/EM-0127P

This document represents one in a series for each of DOE's Operations Offices and Energy Technology Centers. For more information on activities funded through the Chicago Operations Office or its affiliated laboratories, please contact:

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INTRODUCTION

DOE's Office of Technology Development

DOE's Office of Technology Development manages an aggressive national program for applied research, development, demonstration, testing, and evaluation (RDDT&E). This program develops high-payoff technologies to clean up the inventory of DOE nuclear component manufacturing sites and to manage DOE-generated waste faster, safer, and cheaper than current environmental cleanup technologies.

OTD programs are designed to make new, innovative, and more effective technologies available for transfer to users through progressive development. Projects are demonstrated, tested, and evaluated to produce solutions to current problems. Transition of technologies into more advanced stages of development is based upon technological, regulatory, economic, and institutional criteria. New technologies are made available for use in eliminating radioactive, hazardous, and other wastes in compliance with regulatory mandates. The primary goal is to protect human health and prevent further contamination.

OTD technologies address three specific problem areas: (1) groundwater and soils cleanup; (2) waste retrieval and processing; and (3) pollution prevention. These problems are not unique to DOE, but are associated with other Federal agency and industry sites as well. Thus, technical solutions developed within OTD programs will benefit DOE, and should have direct applications in outside markets.

OTD's approach to technology development is an integrated process that seeks to identify technologies and development partners, and facilitates the movement of a technology from applied research to implementation. In an effort to focus resources and address opportunities, OTD has developed **Integrated Programs (IPs)** and **Integrated Demonstrations (IDs)**. An *Integrated Program* focuses on developing technologies to solve a specific aspect of a waste management or environmental problem either unique to a site or common to many sites. Integrated Programs support applied research activities in key application areas required in each stage of the remediation process (e.g., characterization, treatment, and disposal). An *Integrated Demonstration* is a cost-effective mechanism that assembles a group of related and synergistic technologies to evaluate their performance individually or as a complete system, for solving waste management and environmental problems from cradle to grave. In addition to the IDs and IPs, OTD supports crosscutting research and development in the area of robotics. The Robotics Technology Development Program (RTDP) is a "needs-driven" effort. RTDP program activities are funded through most of the DOE Operation Offices and focus on solving site-specific as well as complex-wide environmental problems.

OTD's technology maturation philosophy consists of three components: (1) *technology infusion* - technology transfer from industry, universities, and other Federal agencies; (2) *technology adoption* - shared technology demonstration among DOE laboratories, integrated demonstrations, and programs, and (3) *technology diffusion* - technology transfer from demonstration to industry. To enhance opportunities for technology commercialization, OTD is seeking partnerships with private-sector companies during the technology development and demonstration phases. Industry partners will facilitate implementing these emerging technologies to solve the nation's environmental problems.

Chicago's Contributions

The history of DOE's Chicago Operations Office dates back to 1942, when the first self-sustained, controlled nuclear chain reaction was achieved at the University of Chicago. The next year, the U.S. Army Corps of Engineers' Manhattan Engineer District established a Chicago Area Office to further Manhattan Project work at the University. In 1947, the Atomic Energy Commission established the original Chicago Operations Office. For almost three decades, the Chicago Operations Office participated in research, development, and demonstration projects leading to commercial development of nuclear power, naval nuclear propulsion, and other nuclear technology applications.

Today, the Chicago Operations Office performs energy research and technology development activities in support of the DOE mission. It is responsible for about $2.4 billion in energy research, development, and construction. The office also administers operating contracts for several of the nation's major government-owned laboratories: Ames Laboratory at Iowa State University in Ames, Iowa; Argonne National Laboratory–East (ANL), near Chicago, Illinois; Argonne National Laboratory–West, near Idaho Falls, Idaho; Brookhaven National Laboratory (BNL), in Long Island, New York; Fermi National Accelerator Laboratory, in Batavia, Illinois; and the Princeton Plasma Physics Laboratory, in Princeton, New Jersey.

The Chicago Operations Office manages many programs and projects, including assignments in high energy physics, environmental restoration and waste management, nuclear physics, basic energy sciences, advanced reactor safety, conservation and energy efficiency, solar and magnetic fusion energy, and alternate energy. Under DOE's EM program, the Chicago Operations Office conducts waste research, waste management, and site remediation and restoration activities for all its major facilities. Remediation projects address cleanup of contaminated soils, groundwater, and facilities from past activities. Waste management addresses waste minimization, treatment, storage, packaging, and transportation.

Polyethylene Encapsulation

DOE has begun the formidable task of cleaning up its low-level radioactive, hazardous, and mixed wastes from nuclear weapons development and production. The waste must be characterized, retrieved, and treated to reduce human health and environmental hazards. Before disposal, the waste requires stabilization to prevent contaminants from migrating into the environment. Traditionally, these wastes have been treated with hydraulic cement because it is relatively inexpensive and readily available. However, constituents in the waste can potentially interfere with the chemical reaction required for cement solidification. They may degrade waste forms under storage and disposal conditions, leading to an increased release of toxic materials into the environment.

Polyethylene encapsulation, a technology under development at BNL, may be a safer, more efficient way to dispose of radioactive, hazardous, and mixed wastes. This technology solidifies low-level radioactive waste in polyethylene, an inert thermoplastic material. The encapsulation process heats the polyethylene above its melting point, mixes it with waste, and allows it to cool. The result is a contained, solid waste form. Since it operates at relatively low temperatures, and does not rely on chemical reactions to solidify, polyethylene encapsulation has a number of advantages compared with conventional processes. It can be applied to a variety of DOE and commercial mixed wastes, including nitrate salts, sludges, incinerator ash, ion exchange resins, and sodium sulfate/boric acid. Comprehensive waste form performance testing has demonstrated compliance with regulatory criteria established by DOE, the Nuclear Regulatory Commission, the Environmental Protection Agency (EPA), and the Department of Transportation.

Bench-scale testing showed that the process exceeded minimum performance standards and performed as well or better than traditional solidification technologies. More recently, the technology was subjected to a production-scale feasibility study. Work is continuing to confirm the treatability of various mixed waste samples.

A full-scale demonstration of this technology is planned at BNL's Environmental and Waste Technology Center. All facets relating to successful production will be demonstrated, including: (1) pre-treatment of aqueous wastes using a production-scale stirred vacuum dryer, (2) waste transfer/handling, (3) loss-in-weight metering, (4) extrusion processing, (5) on-line monitoring of waste loading (provided by Ames Laboratory), and (6) process control and data acquisition.

BNL scientists are engaged in other research in the area of stabilization of waste forms. Related projects include in situ containment and stabilization of buried waste, mixed waste treatability-thermoplastic final forms, and conversion of materials containing asbestos into a nonregulated form.

Minimum Additive Waste Stabilization (MAWS)

DOE has sixteen sites that are listed on the National Priorities List (NPL). These sites have sludge pits, evaporation ponds, injection wells, rubble pits, and other sources of contaminated soil and groundwater that need to be remediated. In addition, stored (tanks, barrels, casks) and newly generated wastes need treatment and stabilization into a final waste form before disposal. Cementation of these waste streams has been shown to be ineffective in the long run. Vitrification has been used as an alternative treatment approach, but the quantity of these waste streams is so high that conventional vitrification approaches may be too expensive.

MAWS may provide an environmentally sound alternative for DOE low-level radioactive and mixed waste. Researchers at ANL have used multiple waste streams as substitutes for additives which are utilized for vitrification to produce a stable, high quality waste form, which results in a minimum waste volume for disposal. Integrated systems are used, including vitrification, thermal destruction, soil washing, gas scrubbing/filtration, and ion-exchange wastewater treatment. Durability testing of glass from the vitrification process is also underway.

DOE's Office of Environmental Restoration is expected to be the primary user of the MAWS technology. Tests will begin on pit wastes, contaminated soils and groundwater, and other waste materials at DOE's Fernald Environmental Management Project, in Ohio. MAWS concepts have been applied at the lab- and bench-scale to a waste stream generated at the Y-12 Plant, at Oak Ridge, Tennessee. Process sludges from DOE's Rocky Flats Plant, in Colorado, and solar pond waste will also be evaluated for application of MAWS.

ANL staff are pursuing other breakthroughs in the area of chemical treatment. Work is ongoing in reactive metals treatment, non-aqueous phase liquid (NAPL) remediation using foam, in situ magnetically-assisted chemical separations, and phosphate bonded chemical waste forms. ANL scientists are also working in the areas of program evaluations and assessments.

Characterization, Monitoring, and Sensor Technologies

In order to design an effective remediation approach for contaminants, site characterization is required. Site characterization quantitatively describes the physical components and processes of an ecosystem. It is the first step in any environmental restoration or waste operation activity, and is often considered mandatory throughout the activity.

The traditional approach usually relies on random sampling with extensive off-site analysis and the installation of numerous monitoring wells. Activities such as well drilling, geophysical surveys, and hydrologic modelling are done independently of each other. This prevents daily data integration and delays decision making for the subsequent sampling activity. When conducted this way, the process can take years to produce results because returning to the site several times to eliminate the data gaps is a necessity. Even then the data quality may be inadequate for proper remedial design and action. Consequently, the process typically requires numerous cycles of sampling and analysis, causing overcost and delayed deadlines.

DOE's Characterization, Monitoring, Sensor Technology Integrated Program (CMST-IP) is funded by EM-50 and coordinated by Ames Laboratory. Its mission is to develop new technologies or to reconfigure existing ones for environmental applications for addressing high priority environmental management needs of DOE. Ames Laboratory is working with Iowa State University's Center for Advanced Technology Development to develop usable characterization techniques and sensor technologies.

The Ames Expedited Site Characterization (ESC) project fields innovative characterization technologies, amenable to ESC, along side state-of-the-practice technologies to evaluate their relative added value claims. This is done at actual sites with their associated stakeholders and regulators who can influence the acceptance of these new technologies and this new methodology.

Ames Laboratory has devised a self-contained mobile demonstration laboratory for environmental screening technologies. An Inductively-Coupled Plasma-Mass Spectrometer integrated with a laser ablation sampling system, installed within the mobile lab, has been used to analyze soils at a DOE site in Gunnison, Colorado. The mobile laboratory can be transported across the country and can be operationally ready in several hours.

Ames Laboratory is also designing a portable sensor system to analyze in situ contamination. The system is smaller, less costly, portable, and less sensitive to external environmental factors. Commercial markets may exist for the product. Field-deployable gas sensors are also being developed for use for in situ monitoring of gases in underground storage tanks and at remediation sites. Methods are under study using Fourier-transform infrared photoacoustic spectrometry (FTIR-PAS) to analyze tank waste sludges and solids at DOE's Hanford site in Richland, Washington. FTIR-PAS can analyze milligram-sized samples with little or no sample handling. Transient infrared spectroscopy, a related technology, has been used as a real-time, on-line monitor for polymer encapsulation of low-level radioactive waste salt. This technology has been successful in monitoring the polymer encapsulation process during bench-scale testing at BNL and the Rocky Flats Plant.

Volatile Organic Compounds in Arid Soils Integrated Demonstration (VOC-Arid ID)

Integrated demonstrations are part of DOE's innovative program to speed up development and testing of new technologies for cleaning up hazardous and radioactive wastes. The VOC in Arid Soils ID focuses on technologies to clean up VOCs and associated contaminants in soil and groundwater at arid sites.

The initial host site is located at Hanford's 200 West area.

The primary VOC contaminant is carbon tetrachloride, in association with heavy metals and radionuclides. An estimated 1,000 tons of carbon tetrachloride were disposed of at Hanford between 1955 and 1973, resulting in extensive soil contamination and a groundwater plume that extends more than seven miles.

The VOC-Arid ID is demonstrating technologies in five major areas: (1) site characterization; (2) retrieval and ex situ treatment of contaminants; (3) in situ destruction or immobilization of contaminants; (4) remediation system design and evaluation; and (5) enhanced drilling. This ID is linked directly to an Expedited Response Action, a cleanup effort that focuses on rapid removal of carbon tetrachloride from the soil. A top priority is transferring new technologies to meet the needs of other arid sites. Success will be the transfer to industry of technologies that are ready for immediate use.

In Situ Remediation Integrated Program (ISR-IP)

The In Situ Remediation Integrated Program was instituted out of recognition that in situ remediation could fulfill three important criteria:

- Significant cost reduction of cleanup by eliminating or minimizing excavation, transportation, and disposal of wastes.
- Reduced health impacts on workers and the public by minimizing exposure to wastes during excavation and processing.
- Remediation of inaccessible sites, including:
  - deep subsurfaces.
  - in, under, and around buildings.

Buried waste, contaminated soils and groundwater, and containerized wastes are all candidates for in situ remediation. Contaminants include radioactive wastes, volatile and non-volatile organics, heavy metals, nitrates, and explosive materials. The ISR-IP intends to facilitate development of in situ remediation technologies for hazardous, radioactive, and mixed wastes in soils, groundwater, and storage tanks. Near-term focus is on containment of the wastes, with treatment receiving greater effort in future years.

Efficient Separations and Processing Integrated Program (ESPIP)

DOE sponsors research and development in advanced radiochemical separations to reduce the volume of high-level waste that must be disposed of in deep geological repositories, and to cut the toxicity and volume of low-level acceptable for near-surface disposal. These research and development activities are sponsored throughout the DOE Office of Technology Development ESPIP. ESPIP also develops separation processes to extract high-value materials and non-radioactive hazardous components form nuclear waste and will transfer separations processing to commercial markets.

ESPIP research and development activities are designed to remove radionuclides and hazardous material and chemicals from radioactive defense waste. Radionuclides and other materials under consideration for separation include transuranic elements, such as neptunium, plutonium, americium, and cerium, highly radioactive elements (Strontium-99 and Cesium-137), and long-lived soluble fission products, including technetium-99 and iodine-129. Separation processes will also be developed to extract the long-lived soluble activation product carbon-14; aluminum, phosphorous, and chromium, and the elements that degrade borosilicate glass waste forms; the strategic metals rhodium, palladium, and ruthenium; and Resource Conservation and Recover Act (RCRA) elements and compounds.

The program oversees efficient separations research and development for DOE sites. Current priorities are the cleanup of high-level waste in underground storage tanks (UST) at Hanford Production Operation, Hanford, Washington, and the cleanup of high-level waste at Idaho National Engineering Laboratory (INEL), Idaho Falls, Idaho. Many of the technologies developed for high-level waste will be applicable to other waste streams throughout the DOE Complex and ESPIP will transfer technologies as appropriate.

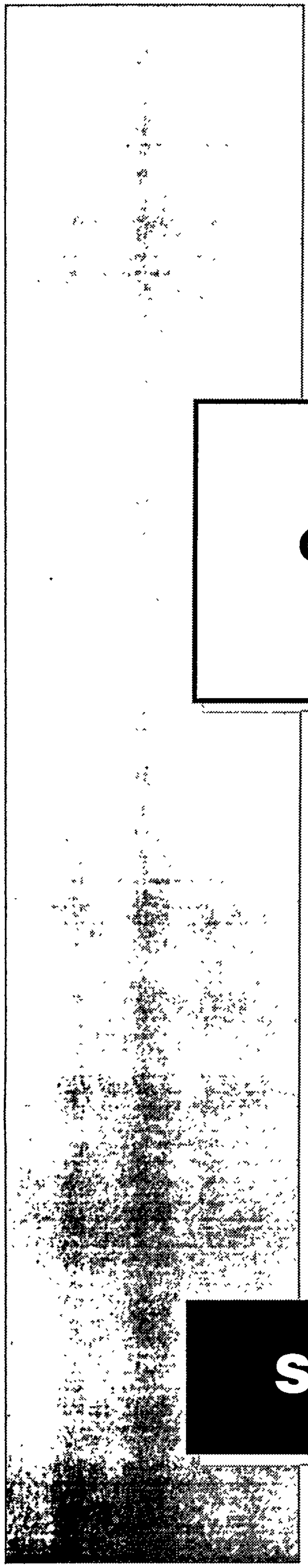
Tank Waste Retrieval Robotics Test Bed

Emptying the USTs is a technically challenging task made difficult because of the hazardous nature of the tank contents. This waste material is chemically complex and includes physical forms ranging from thick, sticky sludge to a crystalline saltcake. The sludge has a consistency of soft mud and the saltcake approximates low-grade concrete. Most of the tanks also contain small amounts of liquid.

Pacific Northwest Laboratory (PNL), Oak Ridge National Laboratory (ORNL), and Sandia National Laboratory (SNL) are working together with the OTD to develop an advanced robotics retrieval system that will use robots - remote manipulators to get into the tanks to break up and remove the sludge and solidified waste. Since the project is technically complex, and because hazardous materials are involved, the development team is creating a full-scale, realistic mock-up of the tank structure.

The facility, located at Hanford, will be used to test and fine tune all major subsystems of tank retrieval robotics using harmless simulated waste forms. The facility will use a 75 by 100-foot wide self-supporting platform that sits over the ground surrounding the underground tank. The platform supports the "long reach manipulator," a robotics arm that positions and operates waste-dislodging tools within the waste storage tank. Researchers hope to start using the test bed facility in 1994, with plans for it to become fully operational in 1996.

The project has several important objectives: (1) to explore the capabilities of retrieval manipulator systems and acquire data necessary to develop specific remediation equipment and techniques; (2) to provide performance guidelines for large manipulator-based retrieval systems; (3) to improve the productivity and safety of such systems by first using them in a non-hazardous environment; and (4) to reduce costs for long-term national remediation requirement. Developers expect lessons learned from this testing to have applications to nuclear waste sites throughout the country.



Groundwater and Soils Cleanup

Section 1.0

1.0 GROUNDWATER AND SOILS CLEANUP OVERVIEW

Some of the most pressing environmental restoration needs for DOE involve cleanup or containment of radioactive and hazardous contaminants (including heavy metals and toxic organic compounds) in soils and groundwater. Sources of this contamination include previous disposal of contaminated wastes in ponds, seepage pits, trenches, and shallow land burial sites; spills and leakage from waste transport, temporary storage facilities, and underground storage tanks; and unregulated discharges to the air and surface waters. EM soils and groundwater programs are designed to identify, develop, and demonstrate innovative technology systems capable of removing or reducing potential health and environmental risks resulting from these previous storage and disposal practices.

Volatile Organic Compound (VOC) contamination of soils and groundwater is one of the most common environmental problems in the United States and the DOE Complex. When VOCs are released into the soil, they rapidly migrate throughout the environment, forming large plumes that eventually result in contaminated groundwater. Two of the more prominent examples of VOC contamination can be found at the Savannah River Site (SRS) (a non-arid environment) where there is a plume larger than three square miles; and at the Hanford Site (an arid site), where an eleven square kilometer mile plume resulted from the disposal of an estimated 580-920 metric tons of carbon tetrachloride between 1955 and 1973. Over 220 sites with similar contamination have been identified in arid environments within the DOE Complex. Add radioactive contamination to these hazardous constituents and the result is a DOE problem for which few adequate remediation solutions exist. Complicating remediation efforts further is the fact that techniques for accessing and removing contaminants differ in arid and non-arid environments. As a result, technologies must be demonstrated and evaluated at multiple sites.

Also prevalent throughout the DOE Complex is the contamination of surface soils with heavy metals resulting form weapons assembly and testing processes during weapons production. At the Nevada Test Site, over 5-square miles of soil is contaminated with plutonium. Cleanup of this area will require the treatment of approximately 25 million cubic feet of soil. Five other DOE sites have similar plutonium-contamination problems and eight other DOE sites have identified problems associated with uranium-contaminated soils. At Fernald near Cincinnati, Ohio, uranium has been transported by rain and snow to varying depths below the surface, making remediation difficult. Estimates indicate there are 1.5 million cubic meters (m^3) of uranium-contaminated soil at Fernald. Heavy metal contamination is also a problem in surface and groundwater. The Berkeley Pit at Butte, Montana, contains 17 billion gallons of contaminated water, with an inflow of 5-7 million gallons per day of surface water and groundwater.

The contaminants discussed above exhibit high concentration levels, high mobility, and high toxicity, as well as long-term persistence in the environment. For these reasons they represent some of the highest priority problems for which innovative technologies are sought. However, technologies are also under development for treatment of non-volatile organics, dense non-aqueous phase liquids, radionuclides, nitrates and explosive materials. In most cases, non-intrusive or in situ methods (methods that characterize or treat the contaminants in place) for environmental restoration are preferable from technical and regulatory standpoints. From a regulatory standpoint, these technologies are preferable because they minimize (1) harm to the environment, (2) public exposure, and (3) volume of waste. Technically, these methods avoid the risks and costs associated with handling contaminated soils and groundwater. Nevertheless, cases exist for which non-intrusive and in situ methods may not be applicable. Given this circumstance, other innovative technologies must be explored, including extraction, containment, recovery, and processing alternatives that reduce or eliminate environmental and health risks.

One of the biggest challenges facing DOE is effective characterization of contamination in soil and groundwater. Characterization must take place before a contaminated site can be properly prioritized for remediation. To accomplish this, non-invasive, field-deployable methods are being developed that are capable of mapping vast areas at depths up to 250 feet below ground level. Results are three-dimensional images that are valuable tools for proper selection and placement of remediation technologies.

The necessity to develop innovative technologies for characterization and treatment of groundwater and soils is not unique to DOE. Other Federal agencies, as well as private industry, are in need of improved methods for these types of cleanup. The EPA has identified 1,235 sites with sufficient contamination to place them on its NPL. In the past two years, the number of sites entering remedial action has grown steadily.[1] Out of 712 NPL sites with Records of Decision (ROD), an estimated 80 percent require remediation of groundwater, 74 percent need soil remediation, and 15 percent require action to clean up sediments. It is estimated that NPL sites without RODs contain similar types of contamination. In an effort to promote the development of new technologies to expedite clean up of the NPL sites, EPA established the Superfund Innovative Technology Evaluation (SITE) program. DoD is responsible for clean up of its facilities contaminated as a result of training, industrial, or research activities. As of September 1991, DoD identified 7,000 sites that will require remediation. The largest of these DoD remediation sites will result in the treatment of nearly 2.2 million cubic yards of soil. DOE works with the EPA SITE, and DoD programs in a joint effort to expedite remediation of groundwater and soils contamination.

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[1] U.S. Environmental Protection Agency, Office of Policy, Planning and Evaluation, Environment Investment: The Cost of a Clean Environment, EPA-230-11-90-083, November 1990.

1.1 OPTIMIZATION OF SAMPLING STRATEGIES

TASK DESCRIPTION

The primary objective of this project is to provide an approach for guiding sample placement for contaminant delineation. This approach must be capable of assisting in siting vertical soil boreholes, directionally-drilled boreholes, and sampling locations along such boreholes. It should include an easy-to-use data management system that allows new data to be integrated with old, and should be visually displayed with useful graphics on computer screens (see Figure 1.1). Such graphics could include maps of contaminant extent, subsurface "cuts" that show contamination location relative to important geological features, etc. It must quantitate contaminated soil and water, and should also provide estimates of the errors associated with these measurements. The data can be used for determining when enough samples have been taken to accurately delineate contamination.

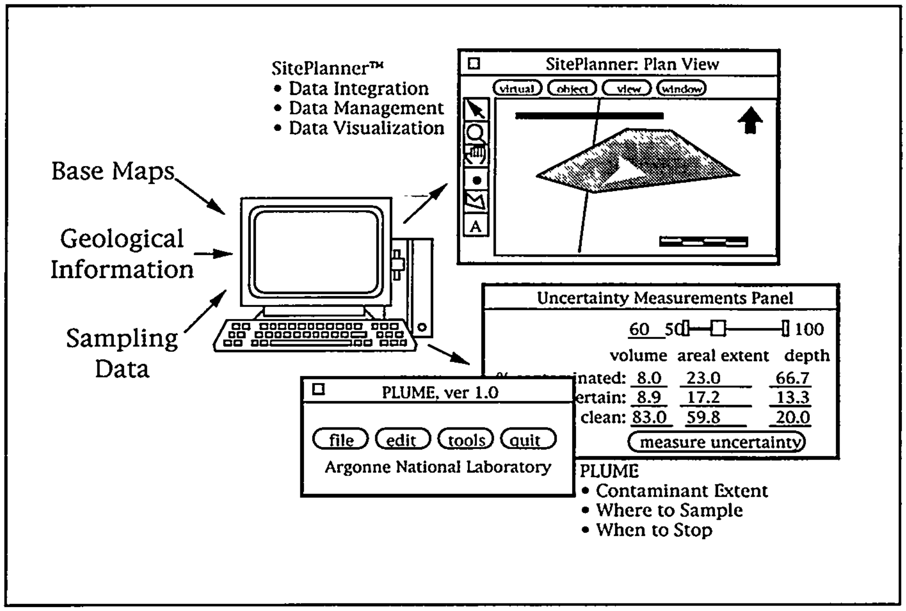

Figure 1.1. Adaptive Sampling Strategy Support.

This project adopts a dual approach to the sampling strategy problem. First, it uses a state-of-the-art object-oriented database system that was specifically designed for site assessment work to integrate, manage, and display site characterization data as it is being generated. This package is called SitePlanner, and was developed by ConSolve, Inc. SitePlanner provides site characterization technical staff with an understanding of their site data as quickly as possible. Coupled with SitePlanner is PLUME, an interactive software package developed at Argonne National Laboratory. PLUME uses advanced statistical procedures to merge "soft" site data with "hard" sample results to form images of contamination location. It also provides quantitative measures of the potential benefits to be gained from additional sampling, and indicates where the best new sampling locations are.

This approach has several advantages over traditional methodologies. In terms of data management and display, SitePlanner provides specialized graphics that are dynamically tied to underlying data. As new data are generated and included in the database, graphics change to reflect the new information. In contrast, traditional Geographical Information Systems (GISs) are limited in the types of graphics they can produce. In the past, specialized graphics packages have not included data management capabilities. SitePlanner was designed as a mouse and menu-driven system that is relatively easy to learn and apply. Traditional GISs and Relational Database Systems (RDBSs) require specialized computer experts to be effective, and are usually not available to the technical staff actually involved with site characterization work.

In terms of data analysis, PLUME readily uses soft data along with hard information to guide sampling strategy selection. This is particularly important for sites in the initial phases of site characterization, when the amount of soft information available typically overwhelms any existing hard sampling results. This capability makes it uniquely different from past sampling strategy selection methodologies. PLUME was designed to address the total sampling strategy problem, including measures of contaminant extent, measures of benefits to be expected from additional sampling, and recommendations about additional sampling locations. Past approaches only addressed one or two of these issues. PLUME has been designed to work tightly with SitePlanner, using a mouse and menu interface. This also makes it easy to use and readily accessible to site characterization technical staff.

TECHNOLOGY NEEDS

Site characterization is an extremely expensive process that typically involves merging information gleaned from historical records, results from field screening sensors, and data generated by laboratory sample analyses. A key step in the characterization of hazardous wastes at DOE sites is determining the extent of contamination. The proper number and placement of sampling locations is required to both minimize characterization costs, and guarantee that contamination extent can be estimated with reasonable confidence. Because "soft" information (i.e., historical records, computer modelling results, past experience, etc.) for a site are usually just as important as "hard" laboratory results, the approach taken must include a quantitative way of accounting for both hard and soft site data.

ACCOMPLISHMENTS

PLUME and SitePlanner were used to delineate subsurface chromic acid contamination at the Chemical Waste Landfill, Sandia National Laboratories. Retrospective studies of characterization efforts at the UNCAP indicate that substantial cost savings could have been realized if an adaptive sampling program (field screening technologies, SitePlanner and PLUME) had been used at this site from the outset. PLUME is currently undergoing commercialization through a Cooperative Research and Development Agreement (CRADA) negotiated with ConSolve, Inc. Future work through the Mixed Waste Landfill Integrated Demonstration (MWLID) includes linking these approaches to risk assessment methodologies at Sandia's Mixed Waste Landfill, and implementing a pilot adaptive sampling program at RB-11, a mixed waste site belonging to Kirtland Air Force Base.

COLLABORATION/TECHNOLOGY TRANSFER

The software is being incorporated into the Sandia Environmental Decision Support System. PLUME software will be commercialized in 1994 by ConSolve, Inc. Site Planner is currently available commercially from ConSolve, Inc.

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1.2 INVERTING MEMBRANE BOREHOLE INSTRUMENTATION TECHNIQUES (SEAMIST™)

TASK DESCRIPTION

SEAMIST™ is an instrumentation and fluid sampler emplacement technique designed for in-situ characterization and monitoring. It uses an inverting, pneumatically-deployed tubular membrane (impermeable material) to deploy sensors and/or samplers in boreholes or to tow instruments downhole in a clean, stable borehole environment (see Figure 1.2).

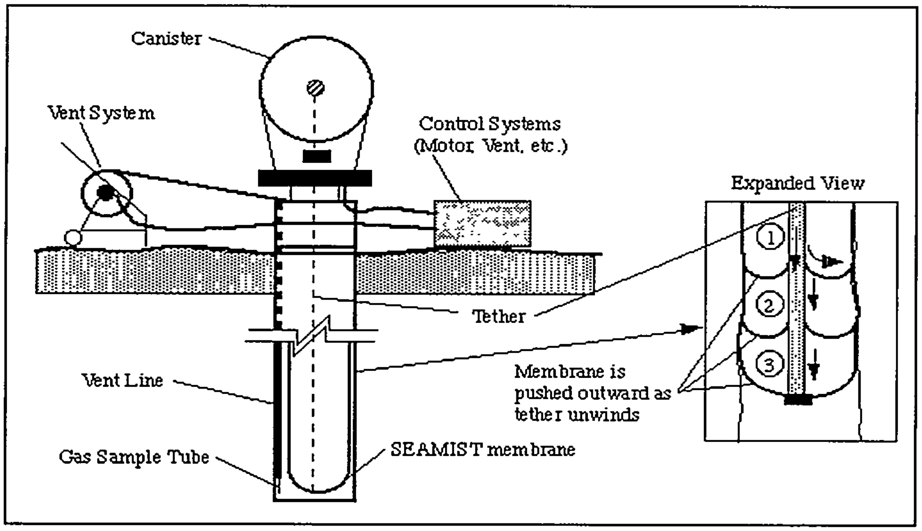

Figure 1.2. SEAMIST™.

The membrane, made of coated fabric or synthetic film, is forced from a holding canister by air pressure into a drilled or punched well. The membrane descends, everts, and presses against the hole wall, providing wall support and the effect of a continuous packer. After emplacement, the entire hole wall is sealed, thus preventing ventilation of the pore space or circulation of pore water in the well. The membrane can be retrieved from the hole.

Permanent installation of the membrane is possible by filling the membrane with grout after emplacement. Semi-permanent installation can be accomplished by filling the membrane with sand after emplacement, which can be removed by vacuuming where membrane retrieval is desired.

Monitoring instruments and pore fluid sampling devices are placed on the outer surface of the membrane, in contact with the hole wall. The membrane isolates each measurement location. Emplacement has been demonstrated for vertical, horizontal, and crooked or partially obstructed holes. Instruments or samplers are not dragged along the hole wall at any time.

The membrane can be used to perform vadose zone pore and fracture fluid sampling using absorbent pads. Electrical resistance measurements inside the pads indicate moisture uptake. By attaching an array of absorbent pads to the membrane, high spatial resolution of the contaminant distribution is possible.

Extraction of soil gas samples from a downhole can be accomplished via tubes to surface sample collectors. Getters (such as activated charcoal adsorbers) can also be attached to the membrane surface to adsorb contaminants. A hybrid concept is to pull a gas sample through a filter positioned at the sampling point.

Additional classes of sensors and/or sampler instruments can be integrated with the SEAMIST deployment system. These include thermocouple psychrometers, gypsum blocks, pressure transducers, temperature sensors, calorimetric indicators, and hydrocarbon-sensitive adsorbing resistors.

TECHNOLOGY NEEDS

Many of the problems with conventional vadose zone monitoring techniques are eliminated or minimized by the SEAMIST™ design. Because it is customizable, retrievable, reusable, and leaves the borehole clean, SEAMIST saves not only time, but also money in drilling costs, tool rehabilitation (rather than replacement and upgrades), and waste stream disposal. It also minimizes or eliminates problems that conventional systems experience, such as retrieval and repair of buried instrumentation, cross-contamination of samples, single-point sampling with screened wells, and borehole stability. The system is ideal for field work, as the device is easily handled and transported. A small unit can fit into the trunk of a car and installation is fast: emplacement in a 100-foot borehole can take less than five minutes.

ACCOMPLISHMENTS

- Tritium Plume Monitoring. Two systems installed at Lawrence Livermore National Laboratory (LLNL) in 1991 are tracking the movement/concentrations of a tritiated water plume (vapor and liquid water sampling) to 40-ft depths.
- Carbon Tetrachloride Monitoring. Two emplacement systems with disposable membrane liners are in use at Hanford for carbon tetrachloride plume monitoring.
- Fracture Flow Mapping and Rate Measurement. Membranes coated with liquid-indicating and wicking layers were used to map and measure brine flows underground at the Waste Isolation Pilot Plant (WIPP).
- Tritium and VOC Sampling. The SEAMIST™ system transported vapor sampling tubes and adsorbent collectors 230 feet horizontally beneath an old radwaste landfill at Los Alamos National Laboratory (LANL).
- Mixed Waste Landfill Demonstrations. Transported logging tools and cameras in horizontal boreholes of up to 230-ft length and 1.75 to 4.0-in diameters. Performed gas sampling and permeability measurements in two vertical boreholes of 11.5-in diameter and 110-ft depth immediately after auguring in SNL's CWL. Installed three borehole liners of 110-ft length.
- Emplaced, operated and removed a vapor sampling membrane in the CWL 60's pit horizontal borehole that incorporated seven sampling points on 170' length, 4" diameter membrane.
- Emplaced, operated (~2 weeks) and removed SEAMIST membranes incorporating physical process and chemical sensors in 110' deep borehole at CWL.
- Standard SEAMIST vapor sampling systems were integrated with surface-based VOC analysis systems (automated/unattended gas chromatograph (GC) and ultraviolet (UV) fluorometer).

- Emplaced and currently operating a 400' long 4.5" diameter vapor sampling membrane in the KAFB RB-11 landfill horizontal borehole.
- <u>Vapor Sampling/Permeability Measurements.</u> Three membranes were instrumented and installed at Savannah River Site (SRS) in July 1992 for soil vapor, vapor pressure, and permeability measurements. Maximum depth was 130 ft, with 10 sampling elevations per membrane.
- <u>Neutron Logging Tool Transport.</u> The membrane towed a 3-lb neutron moisture logging tool in horizontal boreholes. Typically, four 4.5-inch diameter holes (200-250 feet) were logged in one day, with data taken every 2 feet.
- <u>Vapor Sampling.</u> A vapor sampling system was installed to 90-foot depths for long-term monitoring.
- <u>Borehole Liners.</u> SEAMIST™ liners were installed to support/seal holes while a long-term monitoring system is designed. Hole diameter was 8.5 inches and depths were 80-100 feet.
- <u>High-Pressure Borehole Liners.</u> Two Kevlar-reinforced membranes were installed to a depth of 155 feet, then filled with water inside cased walls to prevent collapse of polyvinyl chloride (PVC) casing during remediation experiments.

COLLABORATION/TECHNOLOGY TRANSFER

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The geologic patent for SEAMIST™ was sold to Eastman Cherrington Environmental, Inc. for commercial use in 1993.

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1.3 CONTAINMENT AND STABILIZATION OF BURIED WASTE

TASK DESCRIPTION

This technology aims to develop, demonstrate, and implement advanced grouting materials for in-situ stabilization of contaminated soils and the placement of impermeable, highly durable subsurface barriers. The developmental effort focuses on cementitious and soil cement mixtures compatible with commercially available placement techniques.

TECHNOLOGY NEEDS

Geotechnical engineering and well drilling and completion technologies provide placement techniques for the grouting of fractured media surrounding waste disposal sites and for the in-situ stabilization of waste contaminated soils. Unfortunately, commercially available materials for these applications generally do not meet the requirements for waste site remediation.

ACCOMPLISHMENTS

Formulations for use in an arid environment were optimized and characterized. The major placement techniques considered were jet grouting, soil mixing, and soil sawing. Cementitious grouts with permeabilities of the order of 10^{-10} to 10^{-11} cm/s suitable for monolithic grout subsurface barriers were developed. Permeability after accelerated leaching and repeated wet-dry cycles was of the order of 10^{-10} to 10^{-9} cm/s. The results compare favorably with the EPA permeability limit of 10^{-7} cm/s for landfills.

The developed superplasticized grouts and soil cements have significantly superior mechanical, physical and durability properties than those of conventional formulations. The permeabilities are two to five orders of magnitude less than for other materials frequently used as caps and barriers such as clay, soil-bentonite and cement bentonite slurries. Therefore, the dimensions of the barriers can be reduced significantly.

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1.4 LASER ABLATION/INDUCTIVELY COUPLED PLASMA/ ATOMIC EMISSION SPECTROSCOPY

TASK DESCRIPTION

The focus of this project is to determine the feasibility of utilizing the laser ablation inductively coupled plasma - atomic emission spectroscopy (LA-ICP-AES) technique for determining the existence and extent of radioactive elements in soil, especially uranium, thorium, and plutonium. The LA-ICP-AES technology, used worldwide for the detection of over 70 elements, has been adapted for a mobile analytical facility (See Figure 1.4). Field operable sampling and analysis systems have a great advantage in that samples, especially radioactive samples, need not be collected, catalogued, transported and stored prior to analysis, providing significant savings in analytical costs.

The focused output of a frequency doubled Nd:YAG laser (532nm) is used to ablate unprepared or minimally prepared soil samples. The generated aerosol is entrained in an argon gas flow and introduced into an inductively coupled plasma. The plasma dissociates, atomizes and ionizes the aerosol. The ions may be quantitated by either measuring the intensity of characteristic light emissions (atomic emission spectroscopy), or by introduction of the ions into a quadruple mass spectrometer (MS). Both ICP-AES and ICP-MS are widely used techniques for the determination of a large number of elemental constituents in environmental samples, particularly heavy metals and actinides. They may be used to analyze solids, liquids and airborne aerosols. The LA-ICP-AES technique has been used for the analysis of metals, soils, glasses, ceramics, and powders. Additionally, it is particularly useful for the analysis of nonconducting materials or where sample preparation and handling is either undesirable or impossible.

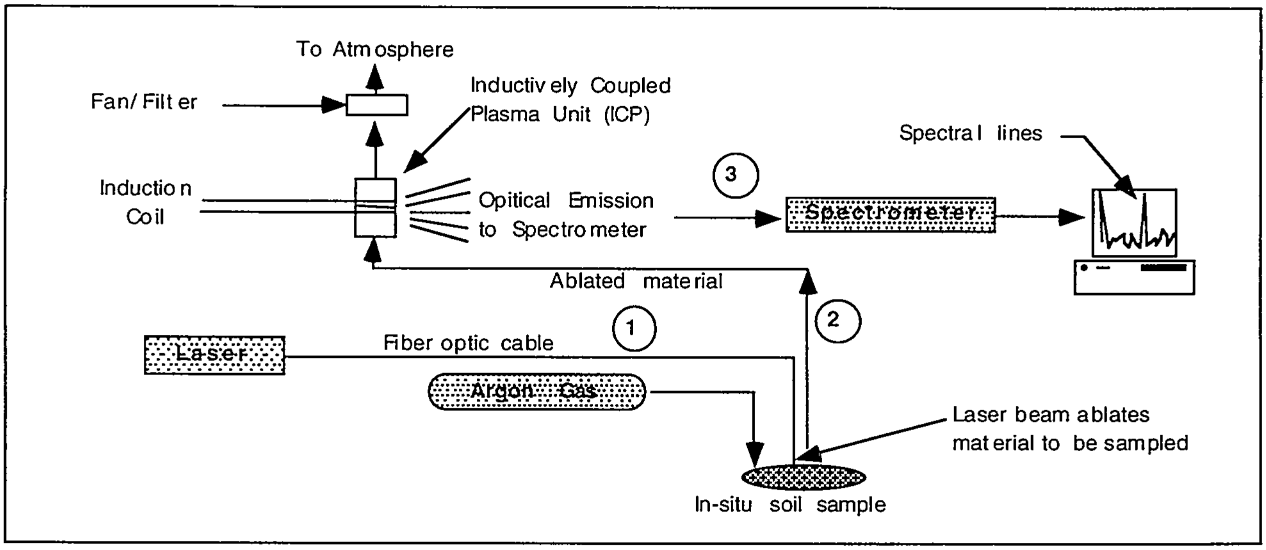

Figure 1.4. The LA-ICP-AES Sample Analysis Technique.

TECHNOLOGY NEEDS

Uranium, actinide and heavy-metal-contamination of soils is a widespread problem in the DOE Complex. Extremely sensitive instrumentation is required to detect contamination down to the levels of required remediation. In order to characterize this contamination over physically large areas of potential contamination, and to monitor the effectiveness of cleanup and decontamination efforts, a field analytical technique is needed that can give real-time measurements to direct cleanup efforts in a timely manner. The LA-ICP-AES technique meets these needs by giving low cost, low detection limit analysis of soil samples in a few minutes per sample with a minimal risk of contamination and exposure.

ACCOMPLISHMENTS

- Demonstrated LA-ICP-AES technique at Fernald, Ohio, in September, 1992.
- Demonstrated in situ analysis of soils at the FEMP plant area for uranium contamination using a mobile laboratory assembled by Ames Laboratory.
- Contamination in the area surveyed near the wastewater treatment facility was generally at or below the identified remediation level, although some higher levels of contamination were identified.
- Demonstrated LA-ICP technique at Gunnison, Colorado in November, 1993 at an Uranium Mill Tailings Remedial Action (UMTRA) remediation site. However, the species of interest was Th-230 in the presence of a large excess of Th-232, and the decision level for remediation was less than 1 ppb, much lower than the 35 ppm level for uranium at Fernald. Therefore, a Perkin-Elmer ELAN 5000ICP Mass Spectrometer was required for isotope resolution and much higher sensitivity. This system was acquired on loan from Perkin-Elmer. The demonstration showed sufficient sensitivity and selectivity to meet the needs of the UMTRA program.

COLLABORATION/TECHNOLOGY TRANSFER

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1.5 EXPEDITED SITE CHARACTERIZATION AT DOE FACILITIES

TASK DESCRIPTION

A technically innovative approach to environmental site characterization has been developed that integrates all appropriate scientific disciplines to provide a more cost- and time-efficient answer for DOE's site characterization needs. The Expedited Site Characterization (ESC) process, developed by Argonne National Laboratory (ANL), emphasizes the use of a variety of non-intrusive or minimally-intrusive technologies (surface geophysics, cone penetrometer, HydroPunch sampling, vegetation sampling, etc.) to optimize sampling locations and minimize monitoring well installation. Technologies are selected on the basis of site-specific problems and requirements. The results of these technologies are often analyzed, interpreted, and integrated on-site by a full team of scientists through the use of a dynamic work plan. Decisions on sampling and analysis requirements are made daily and used for planning the next day's program. This approach has cut the time necessary for full site characterization from programs lasting many months or years, to a matter of a few weeks (see Figure 1.5a).

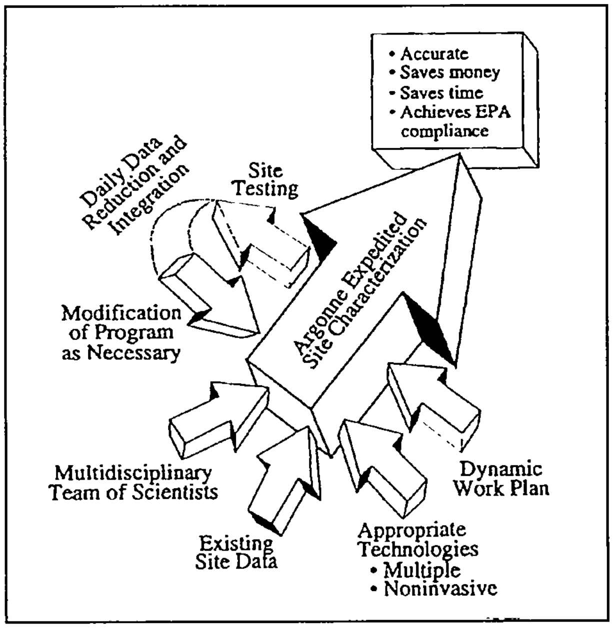

Figure 1.5a. Expedited Site Characterization.

TECHNOLOGY NEEDS

With the increased pressure on Federal agencies and regulators to accelerate the remedial activities and final cleanup of Federal facilities across the nation, there is a growing need to broaden the approach to characterize entire facilities, rather than proceeding one-by-one through the evaluation of the thousands of smaller CERCLA sites or Resource Conservation and Recovery Act (RCRA) -defined waste units. In response, DOE has identified the need for new site characterization technology and approaches as one of its highest priorities. The objective of the ESC process is to provide a more efficient, scientific, innovative, and integrated approach to solving DOE's site characterization needs, and ultimately to clean up sites and facilities across the DOE Complex.

ACCOMPLISHMENTS

During FY93, a demonstration of the ESC process was performed by ANL at a former facility site of the Commodity Credit Corporation, U.S. Department of Agriculture, in York, Nebraska. Prior to field demonstration of the methodology, an ESC work plan specific to the chosen site was developed. The program emphasized the maximum use of non-intrusive technologies, field analytical procedures, and daily integration of data via various computer programs. Private industry and universities participated in the demonstration as needed, providing certain services, such as cone penetrometer, auger drilling, and field analytic capabilities. More than 100 representatives from private industry, DOE, and other government agencies attended the field demonstration. The field demonstration lasted approximately three weeks and included three separate demonstration sessions.

On the basis of the successful completion of the field demonstration, discussions have been held during the first half of FY94 with representatives from EM-50, EM-40, and their contractors to select a site for implementation of the ESC process at a DOE facility. The Pantex Plant has been tentatively selected as the first DOE site (see Figure 1.5b). Appropriate documents related to previous investigations are being reviewed as a prerequisite to development of the technical work plan for the Zone 12 Groundwater ESC.

COLLABORATION/TECHNOLOGY TRANSFER

The ESC process will be transferred to DOE sites for application in the ongoing environmental restoration programs. During the first phase of the transfer process, a pilot program will be implemented at a selected portion of the Pantex Site in Amarillo, Texas.

In addition, as a second phase of the technology transfer activities, training, guidance, and oversight of a selected industry partner at an additional DOE site will be provided. The private company will be responsible for actual implementation and ANL will provide appropriate technologies and the scientific approach of the ESC process.

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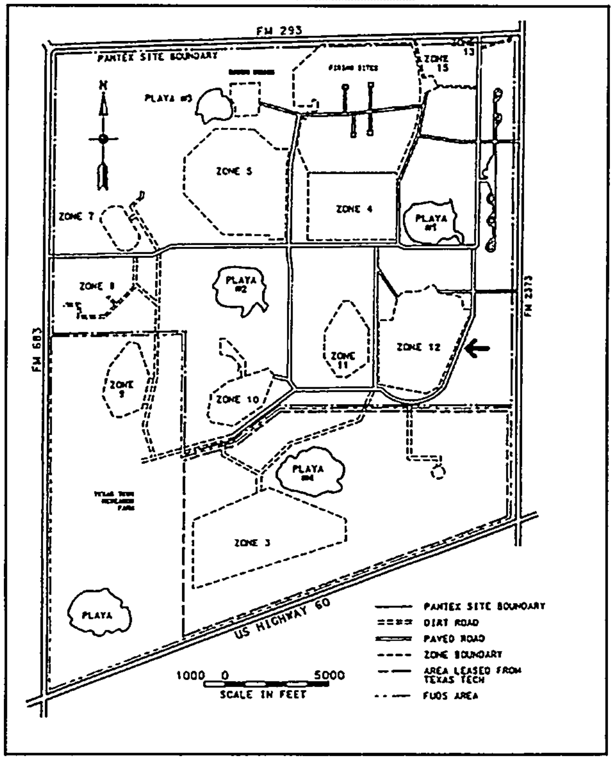

Figure 1.5b. A general map of the Pantex Site showing the locations of current work zones.

1.6 AMES LABORATORY EXPEDITED SITE CHARACTERIZATION PROJECT

TASK DESCRIPTION

The mission of the Ames Technology Integration Program (TIP) was conceived in 1990 as a way for the DOE OTD to exploit the existing Iowa State University (ISU) capability for novel university/national laboratory technology derisking and transfer embodied in the ISU Center for Advanced Technology Development (CATD). "Derisking" is the classic period in the development cycle lying in time between laboratory demonstration (bench-top, test tube, working model) and field (breadboard, prototype, pilot-plant) demonstrations. Scale-up issues can be critical. Technical issues, cost, performance, repeatability, and utility are all issues that may surface. This is especially true in the environmental marketplace where regulations are the dominant market driver. This technology transfer method was recently recognized by the Atlantic Council as one that ought to be used nationwide (see Figure 1.6).

The other major component of this proposal is grounded in ESC, which has several distinctive features. An intensive site investigation occurs over a period of several months that includes a comprehensive search for all existing site documentation and interviews with site personnel. This is the first of several steps that gathers, evaluates and integrates all site information and culminates into a daily integration of field data as a powerful decision making tool based on the human expert analysis of the dynamic site model. Field instruments capable of satisfying the EPA Level III data quality objectives are required for this process to succeed. Multiple, minimally intrusive, hydrogeological techniques are important tools. Careful planning by qualified experts who manage the field activities is at the core of this process from start to finish. The goal is to sufficiently understand the hydrogeologic media as well as the contaminants, so that expensive monitoring/extraction wells can be effectively positioned and successful remediation accomplished.

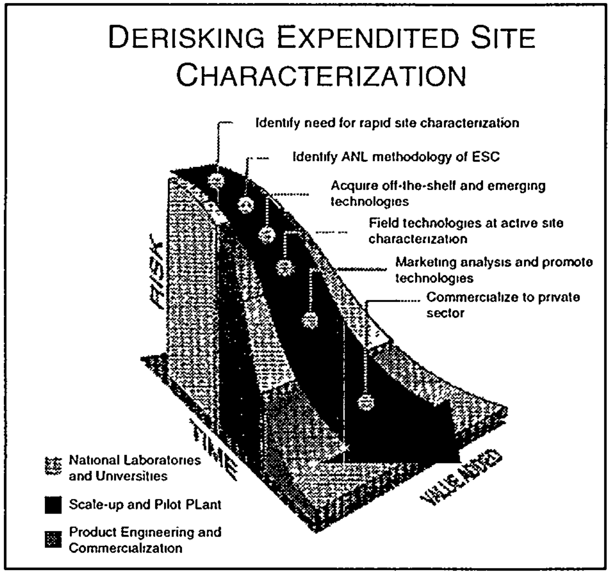

Figure 1.6. Iowa State University Center for Advanced Technology Development Model applied to Expedited Site Characterization.

TECHNOLOGY NEEDS

The objective of this project is to use the ESC methodology as an effective engine for accelerated transfer of site characterization technologies. To do this, actual contaminated sites must be characterized using both state-of-the-practice technologies (SOPT) and emerging technologies (ET) simultaneously. A guiding principle of this task will be to engage the private sector in the fielding of the SOPTs and to seek out the ETs wherever they can be found, whether in the private sector, inside DOE or other Federal agencies, or in university laboratories. Three technology areas are to be fielded and evaluated. Data fusion takes all the site historical information and integrates it with the field hydrogeologic and analytical data into an evolving conceptual site model. A spectrum of two-dimensional (including Site Planner used by ANL) and three-dimensional Geographical Information Systems packages on both a personal computer and a workstation will be fielded in a mobile command center to delineate their relative market niches as a function of site complexity. Choices of analytical and hydrogeologic technologies are site dependent.

ACCOMPLISHMENTS

Both sites planned for FY94 have been selected: a coal tar type, state lead site at Marshalltown, Iowa, and the radiologically contaminated St. Louis Airport site (SLAPS), a DOE Superfund Formerly Utilized Sites Remedial Action Program (FUSRAP) site. Site access has been successfully negotiated for both. Requests for proposals for the site work at Marshalltown have been issued and a high-level statement of work has been agreed upon at SLAPS. Recommendations of the Marshalltown advisory teams have been incorporated into the detailed work plan. Within the organic arena at Marshalltown, SOPTs will consist of GC systems in a mobile laboratory that are tuned to EPA methods (i.e., sonic solvent extraction) while quantitative ET extraction methods (e.g., thermal desorption, supercritical fluid extraction and microextraction) will be fielded. Various immunoassay techniques and passive sorber materials for polycyclic aromatic hydrocarbon (PAH) will be evaluated as organic screening techniques. Hydrogeological technologies include both geophysical and well/borehole techniques as well as a cone penetrometer truck (CPT) equipped with tip/sleeve resistance, four probe resistivity and Laser-Induced Fluorescence (LIF) sensors. An innovative reflection seismic technique and new down-hole instrumented probe have been identified for consideration. Preliminary site activity, such as nonintrusive geophysical and PAH screening, is scheduled for mid-March 1994 and the mobile laboratory intensive site characterization is scheduled for the second half of April and early May 1994.

COLLABORATION/TECHNOLOGY TRANSFER

A Ph.D. student and his advisor will be involved with the analysis and interpretation of the CPT information. Since successful bidders for the Marshalltown site field work have not yet been awarded, it is premature to cite collaborators. However, discussions have taken place with more than one potential private sector entity in each of the technical areas and their site-specific subtasks. National experts have been consulted on various aspects of the technology selection process. Cooperation from the property owner, IES Industries Inc., has been outstanding, both on the issue of coordination for the field work that has permitted the Ames Laboratory to meet its schedule to date, but especially in the more difficult promotion tasks of this project.

Technology transfer is at the heart of this project. State and Federal regulators, technology providers, DOE problem holders, and other stakeholders will be invited to witness both site characterizations in FY94. The site reports will contain recommendations on technology status. But well beyond the reports themselves, brokering of those successful technologies will be an active part of this project after the site characterization work has been finished. The ultimate goal is to enhance the adoption, diffusion and transfer of innovative environmental characterization and monitoring technologies throughout DOE.

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1.7 AMES MOBILE LABORATORY PROJECT

TASK DESCRIPTION

The rapid analysis of soil to determine 230Th activity levels using an on-site mobile laboratory at an UMTRA site will speed the remediation task by supplying the needed results required to make remediation decisions in a matter of 20 minutes, instead of the several weeks usually required to obtain the same information using off-site conventional laboratories. The goal of this task is to develop state-of-the-art technologies into prototype instruments that can help DOE cleanup hazardous waste at the Nuclear Weapons Complex better, safer, faster, and cheaper. The mobile demonstration laboratory for environmental screening technologies (MDLEST) is a completely self-contained mobile laboratory (see Figure 1.7).

Computers and control systems, electrical power, water, gases, and other utilities required to operate instrumentation are supplied by the MDLEST. An inductively coupled plasma-mass spectrometer coupled to a laser ablation (LA) sampling system is the current analytical instrumentation installed in the MDLEST for the soil screening demonstration at the Gunnison, Colorado, UMTRA site.

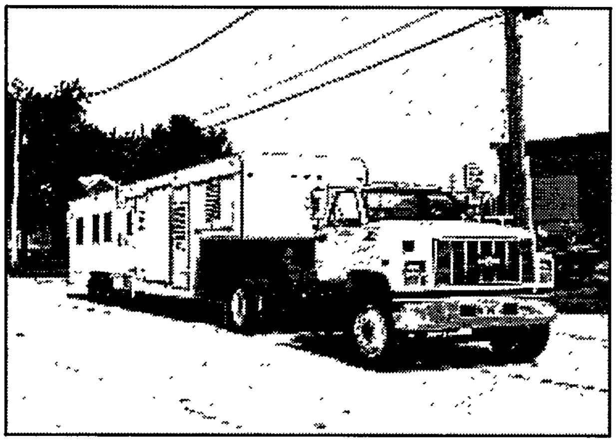

Figure 1.7. The Mobile Demonstration Laboratory for Environmental Screening Technologies.

TECHNOLOGY NEEDS

The current method for determining heavy metals and radioisotopes in soil at the remediation level, as defined by the EPA and the Nuclear Regulatory Commission (NRC) agreements, is to collect a large number of samples and then analyze them using conventional laboratory methodologies at an off-site contract laboratory. Sample turnaround using this method can take several weeks to months, depending on the methodology of analysis used. Moreover, this approach can be extremely costly, not only due to the analysis, but the delays in making decisions on the amount of remediation still required. The rapid analysis instrumentation, LA-ICP-MS, mounted in a mobile laboratory and operated on-site where results are needed for timely remediation decisions, has been shown feasible by the successful demonstration at the Gunnison, Colorado, UMTRA site.

ACCOMPLISHMENTS

The LA-ICP-MS instrumentation has the sensitivity necessary to determine the 230Th activity at the remediation level, 15 pCi/g (0.8 ppb (ng/g)), required by the UMTRA program. Direct analysis of soil samples by LA-ICP-MS in a mobile laboratory on-site allows a few samples per hour to be analyzed to determine the 230Th activity level, which is a more rapid sample turnaround than is currently being achieved using conventional off-site laboratory analyses. While only the 230-isotope of thorium was quantitated at the Gunnison site, the ICP-MS is capable of rapidly detecting trace amounts, sub-ppb, of radioisotopes or other heavy metals in the presence of large amounts of other radioisotopes or heavy metals that might be in the sample and would cause interferences for other measurement techniques.

This demonstration showed that a standard production-model ICP-MS is sufficiently rugged to be installed in a completely self-contained mobile laboratory, be transported across the country, and after arrival at the site, be operationally ready to acquire data in several hours. The system operated in the field for nine days, during winter conditions (as low as -40°F), without a catastrophic failure.

In summary, this demonstration shows the viability of performing rapid, on-site analysis of soil for radioisotopes using LA-ICP-MS as an alternative to current analytical approaches that require several weeks using an off-site laboratory. Given the constraints and severe weather conditions under which this demonstration was performed, the results are promising. Future effort will be directed to the development of sample preparation methods that will enhance the laser ablation particle generation to increase and stabilize the sample particle stream to the ICP-MS, and sampling methodology to increase operational efficiencies. These developments are suggested to provide a state-of-the-art analytical system, with rapid analysis capabilities, to help UMTRA and other DOE programs effectively fulfill their remediation requirements.

COLLABORATION/TECHNOLOGY TRANSFER

The ICP-MS instrument used for sample analysis during this demonstration was on loan from the Perkin-Elmer Corporation. In addition, a Perkin-Elmer Principal Scientist in ICP-MS spent 10 days on the site observing the operation of the ICP-MS in the mobile configuration. The demonstration schedule coincided with the year-end UMTRA meetings at the Gunnison site. Forty UMTRA managers and site personnel were given a tour of the MDLEST system with the LA-ICP-MS in operation. Additional visitors to the site during the demonstration included other instrument manufacturers, contractors, and equipment manufacturers that may be interested in future commercial development of the LA-ICP-MS technology.

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1.8 SITE CHARACTERIZATION AND PENETROMETER SYSTEM

TASK DESCRIPTION

DOE is seeking new technologies to assist in their efforts to characterize and remediate hazardous waste sites under their control. It is DOE's goal to use technologies that will reduce costs and improve quality and timeliness of both site characterization and remediation. To help meet this goal, DOE has purchased a cone penetrometer truck to be used to conduct research and investigations at various sites throughout the country. This system is referred to as a Site Characterization and Analysis Penetrometer System (SCAPS). Figure 1.8 is a diagram of the SCAPS system.

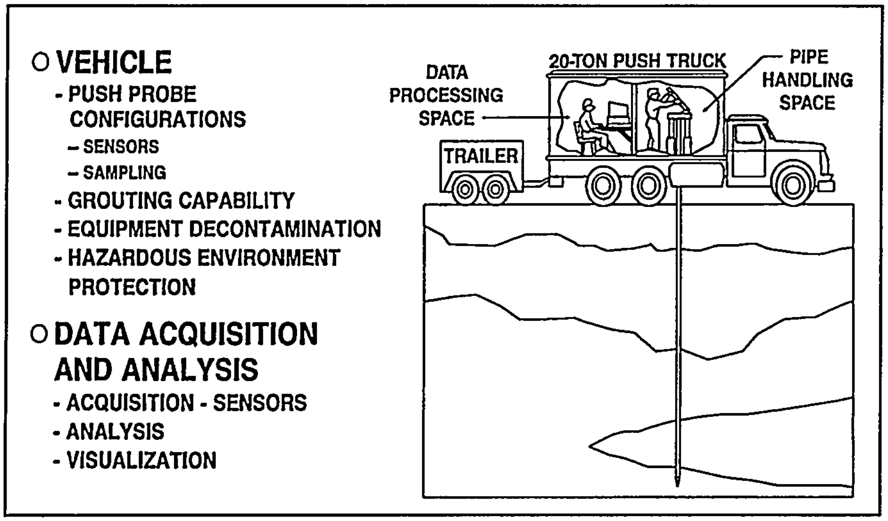

Figure 1.8. Site Characterization and Analysis Penetrometer System description.

DOE's major objective is to operate the SCAPS for evaluation and for further technology improvements to both the vehicle and its components. In addition, it is also DOE's objective to ensure that this technology is then transferred to industry, thus providing a rapid and cost-effective tool for implementation in site characterization investigations at hazardous waste sites throughout the country.

This program will assist DOE in the integration of the SCAPS operations with other facets of OTD's technology development program. Argonne National Laboratory will be responsible for negotiating a contract with a company for the operation and maintenance of the cone penetrometer as well as manage the execution of the subcontract. Technical oversight of the subcontractor will also be provided.

Argonne will be responsible for technical evaluations of all sensors, samplers, and in situ analyses developed. The technology will be evaluated by comparison of the performance to the functional and operating requirements of the potential users of the technology. Once selected the sensor or sampler device will be interfaced to the cone penetrometer.

TECHNOLOGY NEEDS

The SCAPS, and technology associated with its operation, is expected to provide an improved rapid and cost-effective tool to be used in site characterization investigations at hazardous waste sites. The technique will allow in situ measurements of geophysical and physical-properties of soils and stratigraphic units, as well as the determination of the presence of contaminants at a site without the extensive use of drilling and monitoring well installation. The SCAPS will also be used to collect soil and water data that will provide better definition of the zones of contamination enabling more accurate placement of remediation systems and monitoring wells.

An added benefit of the SCAPS is that the potential exposure of site personnel to hazardous materials is greatly reduced because no wastes are brought to the surface. This also reduces the amount of hazardous material that must be controlled and discarded.

ACCOMPLISHMENTS

A technical evaluation team met and reviewed the Request For Proposal responses for the SCAPS operation and maintenance contract. All respondents were evaluated on technical merit, which included experience operating CPT vehicles and equipment and experience with DOE and other government contracts. The team ranked each respondent independently and the technically superior company was selected. The financial office performed a budget analysis on all respondents. A conflict of interest review is being conducted by DOE on the selected contractor and upon completion an award will be made.

COLLABORATION/TECHNOLOGY TRANSFER

This technology will be directly applicable to essentially all environmental groups, whatever their environmental priorities. The products of this project will effect all environmental work including site characterization, site remediation, and site restoration. DOE, DoD, Department of Agriculture, Department of Interior, and the EPA are all potential users of the technology because time and cost will be significantly reduced, and the data collected more comprehensive and accurate. The private sector will also be included as potential users, as corporations begin to realize the need to collect more comprehensive and accurate data at the site characterization phase and speed up remediation of hazardous waste sites. As such, a considerable effort will be directed toward the transferring of information to the scientific community and private sector via literature publications, conferences, and on-site field demonstrations.

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1.9 DEVELOPMENT OF SCREENING AND QUANTITATIVE FIELD METHODS COUPLED TO THE CONE PENETROMETER

TASK DESCRIPTION

The overall goal of this investigation is to develop methods and technology that will couple a cone penetrometer with field-deployable gas chromatography/mass spectrometry instrumentation to directly transfer volatile organic compounds and semi-volatile organic compounds (SVOCs) from subsurface material at depth to the analytical instrument in the field. Sampling, preconcentration, and analytical equipment will be directly coupled to a CPT to provide on-line, near-real-time analyses for VOCs (e.g., trichloroethylene, benzene) and SVOCs (e.g., polynuclear aromatic hydrocarbons, polychlorinated biphenyls) in subsurface materials. Preconcentration devices will be interfaced to GC/MS instrumentation and coupled to sampling devices housed in a CPT for in situ quantitative measurement of VOCs in soil gas and groundwater, and for screening of VOC and SVOC levels in the soil external to the penetrometer wall. The VOCs or SVOCs liberated from subsurface material will be carried to the surface by an inert, heated transfer line, preconcentrated, and analyzed by thermal desorption GC/MS.

TECHNOLOGY NEEDS

The projected costs for hazardous waste site assessment and cleanup in the United States are staggering. Environmental contaminants on DOE sites include radionuclides, toxic heavy metals (e.g., mercury), VOCs, SVOCs, and extractants, such as tributylphosphate. Decisions concerning remediation require reliable information about the presence and extent of contamination at the facilities. The most cost-efficient means of obtaining this information is use of minimally intrusive sampling techniques and on-site (field) analysis of samples. CPTs and in situ groundwater samplers provide a minimally intrusive, efficient, and cost-effective method for obtaining subsurface materials for analysis of contaminants. On-site analysis of samples has been shown to facilitate the characterization of sites by making real-time, interactive sampling decisions possible. Sampling techniques for VOCs in subsurface materials have been developed, and methods that are accepted by the EPA have been reported. These methods, although currently accepted, are cumbersome even when they are applied during on-site analyses. Consequently, there is a need to provide on-line, near-real-time methods of analyses for VOCs and SVOCs in subsurface materials that maintain sample integrity and improve the accuracy of the analytical results by eliminating the manipulation of samples during collection, transportation, and storage.

ACCOMPLISHMENTS

Tests have been initiated to determine the inertness of several different transfer line materials (stainless steel, nickel, Teflon® TFE, and Teflon® PFA) that will carry the VOCs from the CPT to the preconcentration device at the surface. A system has been designed to test transfer line materials in which the relative humidity and temperature of the gas stream carrying the VOCs can be controlled. A gas stream of a fixed relative humidity is generated by mixing dry zero-grade air with a humid air stream flowing from a gas washing bottle containing VOC-free water. The humid air stream is mixed in a stainless steel cylinder with the gas stream from a standard containing the VOCs and drawn through the transfer line with a personal sampling pump. VOCs in the sample steam are collected on graphite carbon and analyzed. Results are compared with the concentrations of VOCs in the mixing chamber to determine if they are retained by the transfer line.

A commercial Teflon® bailer has been purchased and is undergoing modification for incorporation into a CPT for in situ sparging of VOCs in groundwater. Methods are being developed to prepare aqueous standards of the VOCs for use in testing the device. A method will be developed to measure VOCs and SVOCs in soil. In this method, the compounds will be thermally desorbed from the soil adjacent to the CPT wall. The interface to the soil will consist of stainless steel mesh that will be inserted in the CPT in place of the membrane. Heater cartridges will be emplaced into the interface to heat the wall of the penetrometer to sufficient temperature to thermally desorb, but not pyrolyze, the VOCs and SVOCs. The desorbed organics will be swept through the mesh interface into the heated transfer line by an applied vacuum. Methods are being developed to prepare soil standards containing VOCs for use in testing the device.

COLLABORATION/TECHNOLOGY TRANSFER

The basic GC/MS systems to be used in this project are commercially-available, but are not widely applied in environmental characterization work. For this project to be considered successful in terms of providing better, faster, safer, and cheaper technology to EM-40 and EM-30, information about the technology and these results must be made widely available to DOE site users. As part of the effort to gain acceptability, follow-on demonstration of the technology at an integrated demonstration has been proposed. Ames Laboratory is working with the commercial vendor to incorporate hardware and software changes into the instrument, to make the methods available to users as catalog items, and to market the whole package for use at DOE sites. Specific business relationships (e.g., a CRADA) and commercialization plans will be developed as part of this activity. Key to acceptance within the DOE community is acceptance by EPA of the data generated. A plan to gain EPA acceptance of both the field screening and the field quantitative methods will be developed. Results of this research and development will be presented at appropriate scientific meetings and DOE workshops, published in appropriate scientific journals, and published in DOE reports as needed. Distribution will be aimed at DOE site users.

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1.10 LA-ICP-AES USING A HIGH-RESOLUTION, FIBER-OPTIC INTERFEROMETER

TASK DESCRIPTION

A high-resolution, compact, and portable interferometer system is being developed to provide isotopic and isobaric resolution and higher sensitivities for samples in complex matrices where detection limits are limited by low-level interferences. This system will be used in conjunction with environmental analysis by laser ablation - inductively coupled plasma - atomic emission spectroscopy. The technology being developed involves the use of an acousto-optic tunable filter (AOTF) and a high finesse fiber-optic Fabry-Perot interferometer (FFP), two devices developed by the communications industry for high bandwidth laser communications. The small size, extreme ruggedness, and spectral agility of these systems will make them well suited for use in a fieldable spectrometer system at a fraction of the cost, size, and weight of grating-based spectrometer systems. The AOTF will be used as a low-resolution filter to select spectral regions to be resolved by multiple FFP filters (see Figure 1.10a). The AOTF is capable of switching between spectral regions in microseconds with no mechanical moving parts and is also capable of simultaneous selection of several spectral regions.

TECHNOLOGY NEEDS

LA-ICP-AES has previously been shown to be a valuable tool for rapid, in situ environmental analysis. However, some limitations of this technique include sensitivity limited by the resolution of many emission lines for samples having complex matrices, lack of sufficient resolution to determine isotopic ratios for transuranic materials, and excessively large, expensive and temperamental spectrometer systems. The system under development addresses all of these shortcomings with commercially-available components developed for other uses.

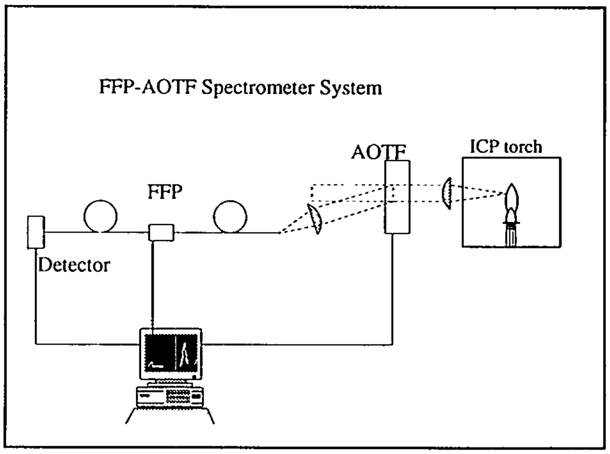

Figure 1.10a. Schematic of the acousto-optic tunable filter, fiber-optic Fabry-Perot interferometer system.

ACCOMPLISHMENTS

An AOTF has been obtained for use in this system and initial tests have been performed using a low-resolution (finesse=100) bulk-optics Fabry-Perot interferometer. A single AOTF accesses a 200 nm range of emission features. The bandwidth of the AOTF (~1,000 GHz) and the desired spectral resolution (~2 GHz) determine the specifications for the FFP (finesse=500) that must be developed to scan the spectral window defined by the AOTF (see Figure 1.10b). The optical coatings used in the FFP will not cover the entire region accessed by the AOTF. Therefore, a system with full access at high-resolution must utilize several FFPs, with a single AOTF for prefiltering and low-resolution survey scanning. The FFP technology to be used is already developed for red and NIR wavelengths, and development has begun for the blue and ultraviolet wavelengths required for this project. A spectrum of a sample containing natural abundances of U 235 and 238 (.7 and 99%) was obtained using the bulk-optics Fabry-Perot (see Figure 1.10c). The higher resolution of the FFP under development will greatly improve the obtainable spectra.

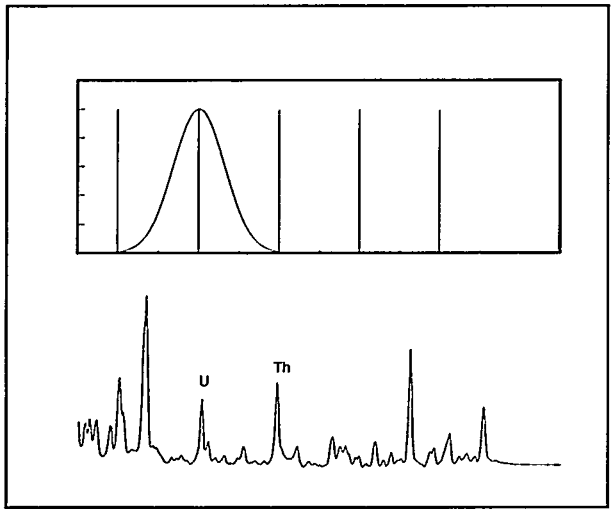

Figure 1.10b. Illustration of overlapping bandwidths of acousto-optic tunable filter and fiber-optic Fabry-Perot devices leading to high resolution of combined system.

COLLABORATION/TECHNOLOGY TRANSFER

This high-resolution interferometer system is capable of resolution comparable to that of commercial 3-meter spectrometer systems at considerably less cost, smaller package size, greater portability, and less sensitivity to external environmental factors. Its potential for use in portable spectrometric systems that require this combination of high-resolution and spectral agility should make this system highly marketable. The commercial developer of the fiber-optic Fabry-Perot interferometer has an established market in the communications industry and is exploring the spectroscopic industry through this collaborative work. Publication of the results of these investigations in spectroscopic and analytical chemistry journals will be the first step in widening interest in this technology. Further utilization of this system in future applications of the LA-ICP-AES and other spectroscopic applications within DOE will illustrate the usefulness of this system.

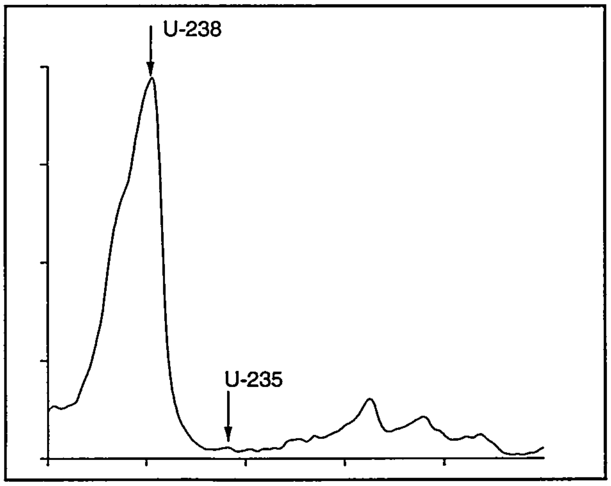

Figure 1.10c. Spectrum of uranium solution in an inductively coupled plasma, using the bulk optics Fabry-Perot.

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1.11 TECHNOLOGY PERFORMANCE SPECIFICATIONS

TASK DESCRIPTION

This project will establish and implement technology performance specifications for Research and Development and Demonstration, Testing, and Evaluation projects within the DOE Office of Technology Development (EM-50). Technology performance specifications will be used to establish milestones, evaluate the status of ongoing projects and determine the success of completed projects. Preliminary performance specifications will be required in Technical Task Plans (TTPs) and will be evaluated as part of the TTP evaluation. In the first year, a pilot project will focus on chemical and radio-analytical measurement technologies for VOCs. The Principal Investigators will prepare a preliminary list of specification topics and values for chemical and radio-analytic measurement technologies. The list will be derived from available sources and resources. Evaluation criteria will address whether the list is complete, whether the values are within regulatory requirements, whether the values are reasonable, and whether the entire system will be workable.

The reviewers comments will be used to revise the specifications, which will then be applied to the three OTD-supported technologies selected by the Headquarters Managers, along with draft guidance to facilitate dissemination of specifications to the affected constituents (e.g., Principle Investigators, Technical Support Groups, etc.). In subsequent years, specifications will be prepared in other technical areas as directed by Headquarters.

ACCOMPLISHMENTS

A Performance Specifications Model has been prepared. The first step of the performance specifications process is to state the need of the environmental restoration or waste management customer. The general approach of the model is to document the baseline technologies that currently exist, or are nearing completion of their development, and to compare the baseline to the customers' needs in order to determine unmet requirements. The unmet requirements form the basis for further technology development. Investigators must be quantitative in assessing their proposed technology's reduction in the current cost of analysis or improvement in analyte detection over established measurement technologies.

A draft DOE report entitled Technology Baseline for VOC Characterization and Monitoring in the Environment has been prepared and distributed. The report reviews the following technologies: gas chromatography, mass spectrometry and gas chromatography, fiber-optic chemical sensors, infrared and Raman spectroscopy, electrochemical sensors and piezoelectric sensors. Included in the review are a description of the basic principles, applications and commercial-availability of instrumentation. In addition, the report also addresses the Performance Specifications Model referred to above.

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1.12 ZERO-TENSION LYSIMETERS: AN IMPROVED DESIGN TO MONITOR COLLOID-FACILITATED CONTAMINANT TRANSPORT IN THE VADOSE ZONE

TASK DESCRIPTION

A lysimeter is a device installed in the soil to periodically sample groundwater. Zero-tension lysimeters (ZTLs) are especially appropriate for sampling water as it moves via preferential flow paths in saturated or unsaturated conditions. Because no ceramic barrier or fiberglass wick is involved to maintain tension on the water (as is the case with other lysimeters), particles suspended in the water, as well as dissolved species, may be sampled with ZTLs. A ZTL design is described to capture samples of suspended colloids as they move in the vadose zone.

The improved ZTL consists of a Teflon or polycarbonate cylinder placed below an undisturbed core of soil that has been initially withdrawn with an hydraulically-powered tube. The design has significant advantages over conventional designs with respect to simplicity and speed of installation. Because more ZTLs of this design can be installed to assess site variability, more accurate monitoring of contaminant transport before, during, and after remediation will be achieved. In addition, because of the improved spatial resolution in sampling and monitoring, if contaminants are mobilized, their source can be more easily identified than with piezometer-based monitoring methods.

The improved ZTL has been installed in 24 research plots near Ames, Iowa, to monitor potential transport of heavy metals applied to the soil in municipal sewage sludge. In 1993, four lysimeters were also installed at a site contaminated with americium and plutonium at the Rocky Flats Plant, Golden, Colorado.

TECHNOLOGY NEEDS

Zero-tension lysimeters are needed to monitor contaminant migration with mobile colloids (see Figure 1.12a.). They are particularly applicable where a site is undergoing in situ remediation treatment that leaves the soil physically undisturbed. They can also be used in other contexts where colloid-facilitated transport of contaminants is suspected or must be quantified in near-surface environments.

A zero-tension lysimeter that can be installed in much less time and with less site disturbance would allow more extensive and therefore more accurate monitoring of colloid transport in contaminated soils. In this project, a design that meets these needs is presented.

ACCOMPLISHMENTS

At the Ames site, turbidity in the soil water collected by the ZTLs was dependent upon the level of sludge addition to each plot. In both 1992 and 1993, the higher the rate of sludge addition, the less turbidity occurred in water that leached through the soil (see Figures 1.12b. and 1.12c). Greater additions of sludge may be limiting colloid transport through the soil because of the abundance of salts added to the soil with the sludge. Greater ionic strength in the soil solution tends to limit

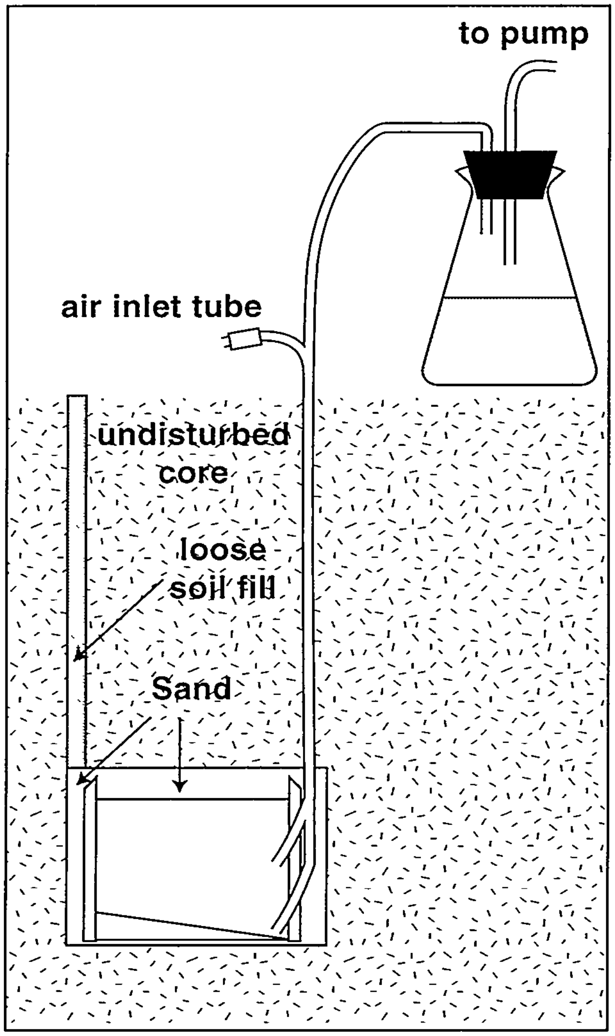

Figure 1.12a. Sampling and maintenance of the zero-tension lysimeter.

expansion of the diffuse layers of ions associated with soil colloids and to keep colloidal materials from dispersing.

This study is being conducted in the first years of sludge additions to the soil, and levels of heavy metals in the soil water were always low. In fact, it was rarely possible to detect cadmium in the water by the ICP-MS technique employed. Levels of zinc and nickel were typically in the ranges of 5 - 20 mg/L, and these concentrations were not clearly correlated with any of the other parameters that were measured.

Copper occurred in concentrations that were low (also typically 5 - 20 mg/L), but copper levels could be correlated both to treatment effects and to other soil water parameters. For example, significantly more copper leached into the ZTLs installed in plots receiving sludge treatment than in control plots. In addition, significantly more copper leached into the ZTLs under switchgrass than into ZTLs under trees. It is hypothesized that the trees are more effective at taking up copper and storing it in the biomass than is switchgrass.

Multiple linear regression analyses indicated a correlation of mobile copper with dissolved organic carbon, pH, turbidity, and phosphorus, although the correlations varied between the two years of the study. These statistics suggest that copper moved through the soil in an organically complex form, consistent with laboratory studies that have demonstrated strong complexation of copper by soil organic matter. The correlation of copper movement in the soil with vegetation and rate of sludge amendment was only possible because an adequate number of ZTLs had been installed at the site to allow for meaningful statistical analyses. Otherwise, the soil's spatial variability and the relatively low levels of copper concentrations in the soil water would have made valid conclusions impossible. The ZTLs installed at the Rocky Flats Plant in 1993 will be tested by using simulated rainfall in the spring and summer of 1994.

COLLABORATION/TECHNOLOGY TRANSFER

The principal investigator works closely with an end user at EG&G Rocky Flats in using the improved ZTLs to characterize the rate of actinide migration at the site. Successful field demonstrations will result in wide acceptability at other sites for monitoring contaminant migration in the vadose zone.

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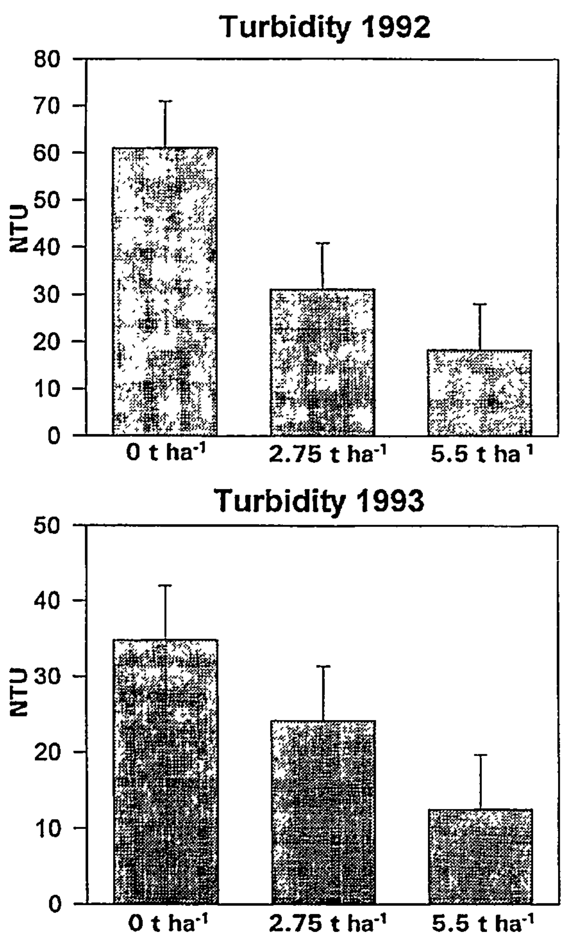

Figure 1.12b. Turbidity 1992.

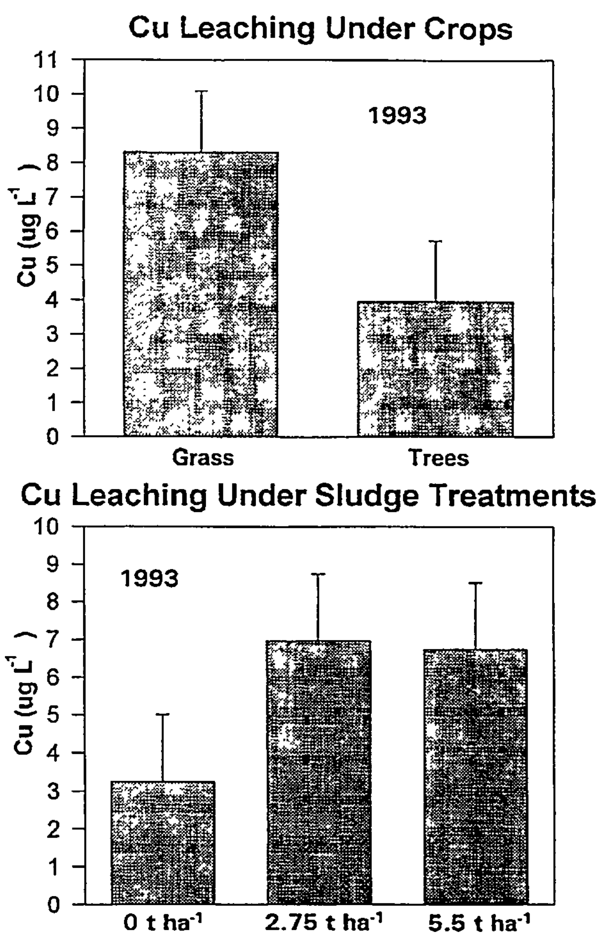

Figure 1.12c. Copper leaching under crops.

1.13 SENSING OF HEAD SPACE GASES: CONTINUOUS IN SITU MONITORING OF GASEOUS COMPONENTS IN UNDERGROUND STORAGE TANKS USING PIEZOELECTRIC THIN FILM RESONATOR SENSORS

TASK DESCRIPTION

This task focuses on the development of semiconductor-device-sized, field-deployable gas sensors for use in the in situ monitoring of head space gases in underground storage tanks (USTs) and remediation sites. The gas sensor system will be comprised of arrays of cost effective, piezoelectric mass sensors and electronic readout instrumentation for the determination of the concentrations of several hazardous gases in the hostile environment of USTs (e.g., hydrogen, ammonia, nitrous oxide). Using integrated circuit technology and specially synthesized sensor surface coatings, small sensor systems capable of long-term, low- maintenance operation will be fabricated as manufacturable prototypes and field-tested to determine operational specifications.

The gas sensors will be developed from existing bulk acoustic-wave piezoelectric mass sensors that will be coated with materials that can selectively sorb the gases of interest. These highly sensitive mass sensors are thin film resonators (TFRs) consisting of thin piezoelectric aluminum nitride membranes in the shape of 400 micrometer squares that are supported by a silicon substrate (see Figure 1.13a). These sensors can detect surface mass loadings lower than 2 nanograms per square centimeter, which is much less than the loading for an adsorbed layer of a typical analyte. Coatings will be developed to withstand the harsh chemical and radiological environment of the USTs.

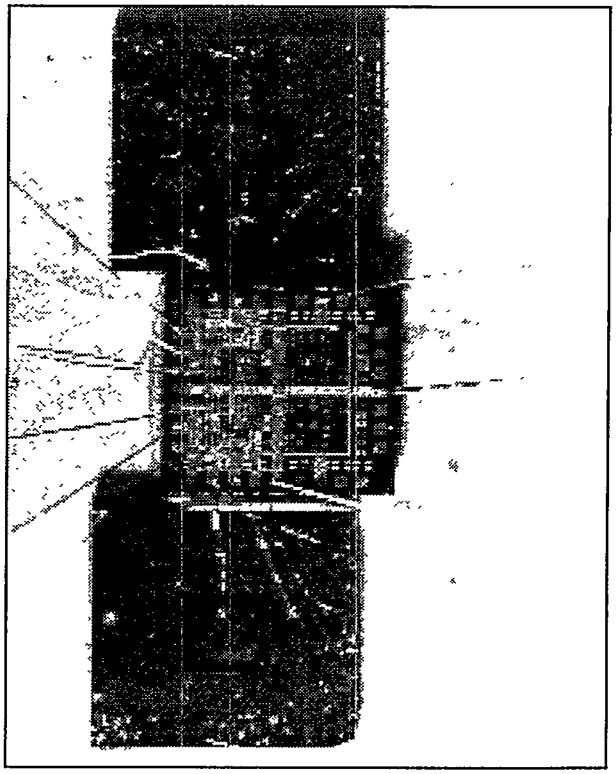

Figure 1.13a. Two thin film resonators and a custom integrated circuit epoxied to a chip carrier.

TECHNOLOGY NEEDS

The head spaces of USTs often contain explosive and toxic gases, such as hydrogen, nitrogen oxides, hydrocarbons, and ammonia. These gases are released from the viscous semi-solid tank content material to potentially provide locally high concentrations of the gases. Knowledge of water vapor content in head spaces is also useful to allow assessment of fire retardant potential. Thus, methods are needed to characterize the release and diffusion of gases within head spaces, and to monitor quantitatively the concentrations of these gases over extended periods of time at many tank sites, as well as at different locations within each tank. Any measurement devices placed inside the tank must not be a spark hazard and must be inherently safe in their operation. The monitoring need especially requires the development of cost effective, inherently safe, readily deployable gas sensors capable of long-term, unattended operation. Use of such devices at Hanford and Savannah River Site and other DOE sites would be especially helpful to field personnel from a safety and health perspective.

ACCOMPLISHMENTS

Work on this task was initiated in April 1993. The following summarizes the status of sensor coating development, integrated system design, and array implementation.

Initial prototype hydrogen sensors were created by depositing different palladium alloys and doped palladium coatings onto the surfaces of quartz crystal microbalances (QCMs) (Coatings are first tested on QCMs and then applied to TFRs). Responses proportional to the square root of the molar concentration of hydrogen can be obtained over two orders of magnitude with the concentration range dependent on the type of alloy or dopant combined in the palladium coating. An example is illustrated in Figure 1.13b. Thus, an array deployment using a selected subset of these coatings can be used to construct a sensor with a large dynamic range. Testing of these sensors for possible interferences from other vapors found in USTs is underway.

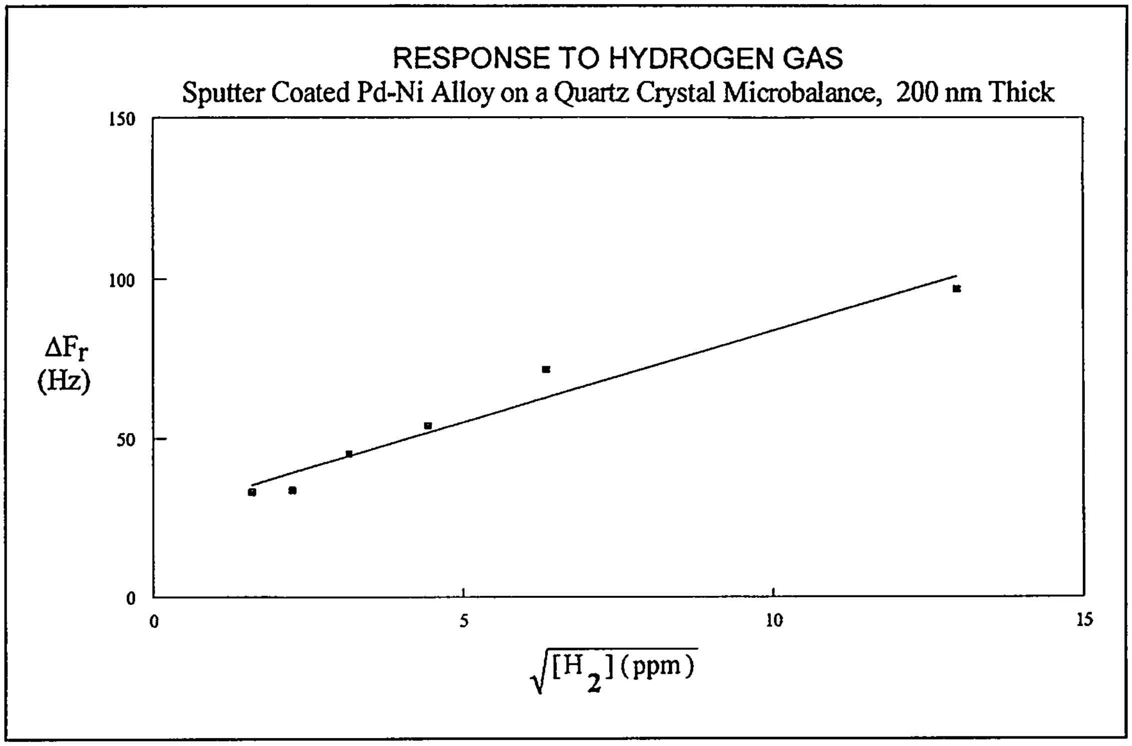

Figure 1.13b. Response of quartz crystal microbalances with a coating of nickel-palladium alloy as a function of hydrogen concentration.

field deployable sensor system is under development. TFRs have been deployed as reference and indicator pairs with partial compensation of nonspecific effects, such as temperature, as indicated in Figure 1.13c. Electronic support circuitry has been successfully designed and implemented using two technologies: custom integrated circuits and discrete surface mount components. The design for a second generation custom integrated circuit to support operation of higher density arrays has been completed.

COLLABORATION/TECHNOLOGY TRANSFER

Upon completion, the field deployable gas sensor system will be useful for the characterization and long-term monitoring of hazardous and toxic gases within and near USTs. Many USTs exist at Hanford, and so preliminary discussions have taken place with Westinghouse Hanford Company and Richland Field Office personnel with respect to the gases and concentrations typically found in USTs, and with respect to making arrangements to field-test the sensor system. Field testing at this site will commence after satisfactory bench testing.

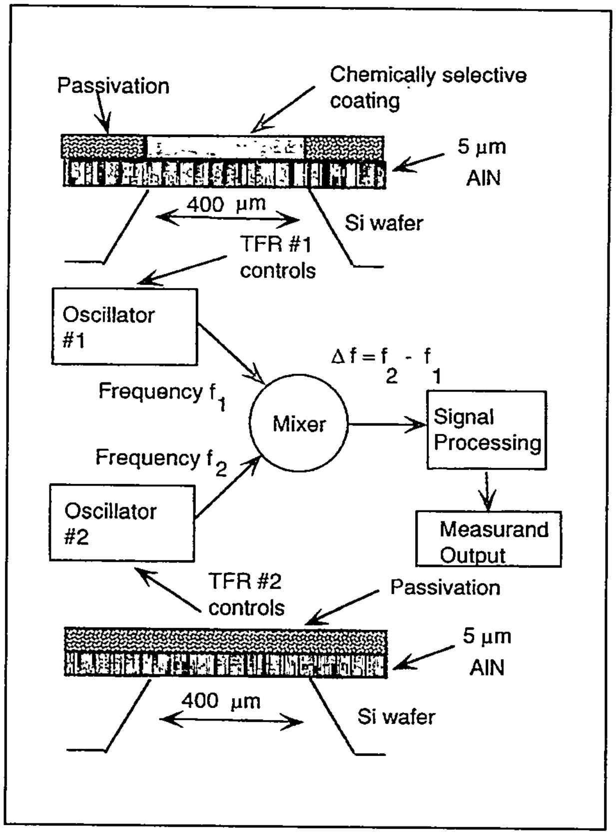

Figure 1.13c. Thin film resonators are used as the frequency control elements in oscillator.

Commercialization of TFRs has been discussed with several corporations to find a partner for manufacturing and systems integration. An option for a license to patented TFR technology has been offered to one company for a portion of the environmental monitoring applications related to DOE needs. Discussions are continuing with other corporations for development of TFR sensors for commercial, as well as other DOE-related, areas.

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1.14 INFRARED ANALYSIS OF WASTES: NOVEL LAB AND ON-LINE MEASUREMENTS BY PHOTOACOUSTIC AND TRANSIENT INFRARED SPECTROSCOPIES

TASK DESCRIPTION

This project consists of two different subtasks, which are developing technologies for separate environmental needs. One subtask is developing an analytical method for the sludges in large storage tanks at the Hanford Site. The other is producing a real-time process-stream monitor for the polymer encapsulation of low-level rad waste salts. The Hanford waste-tank sludges are chemically active and physically heterogeneous, which makes them difficult to analyze by most methods, without extensive sample preparation. The project is developing laboratory methods using Fourier-transform infrared photoacoustic spectroscopy (FTIR-PAS) to quantitatively measure the molecular and multi-atom ionic components in these sludges. Methods have been worked out for the production of consistent samples and quantitative spectra. Calibration and component identification procedures are in preparation. The technology and need-specific methods will be transferred to Hanford personnel principally by training sessions held by project staff at Hanford, but also by providing guidance and advice whenever requested.

The second subtask is applying transient infrared spectroscopy (TIRS) as a real-time on-line monitor for the polymer encapsulation of low-level rad waste salt. Figure 1.14a shows how a TIRS unit will be applied to the waste processing operation. The TIRS monitor was originally developed for real-time analysis of process streams consisting of ambient temperature solid materials. It is being adapted in this project to the high temperature, viscous liquid process stream produced by the encapsulation process. The adapted monitor will be demonstrated in both cold and hot tests at both Rocky Flats Plant and Brookhaven National Laboratory with laboratory and pilot-scale waste processors.

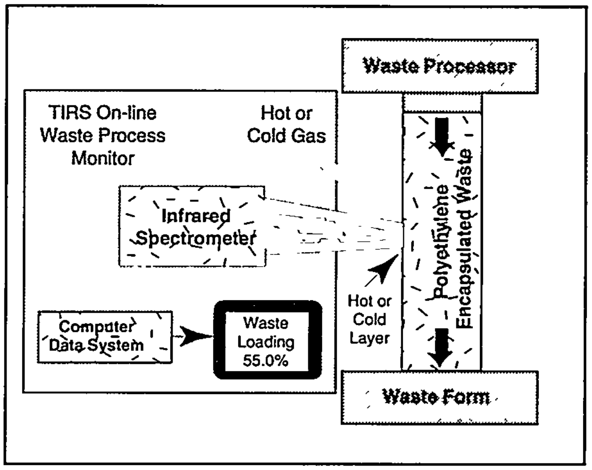

Figure 1.14a. Schematic of a transient infrared spectroscopy unit on the waste encapsulation line.

TECHNOLOGY NEEDS

The waste-tank sludges and solids at Hanford present a uniquely challenging analytical problem. They are physically and chemically heterogeneous, chemically active, and radioactive. FTIR-PAS is exceptionally capable of handling such material. It can analyze milligram-sized samples with little or no sample handling. This increases efficiency, minimizes worker exposure, and reduces waste production. FTIR-PAS will provide a quantitative compositional analysis of the multiatomic ions and molecular species, which are the chemically active components in the sludges and solids. Brookhaven National Laboratory and Rocky Flats Plant are developing the polymer encapsulation process to immobilize radioactive salts and similar wastes for storage and disposal. TIRS appears to be the only technology available that can monitor the process stream in real time. It will provide data that will guide the waste process operators in their control of the encapsulation, certify the composition of the processed waste for regulators, and provide a record of the processed waste should questions or problems later arise.

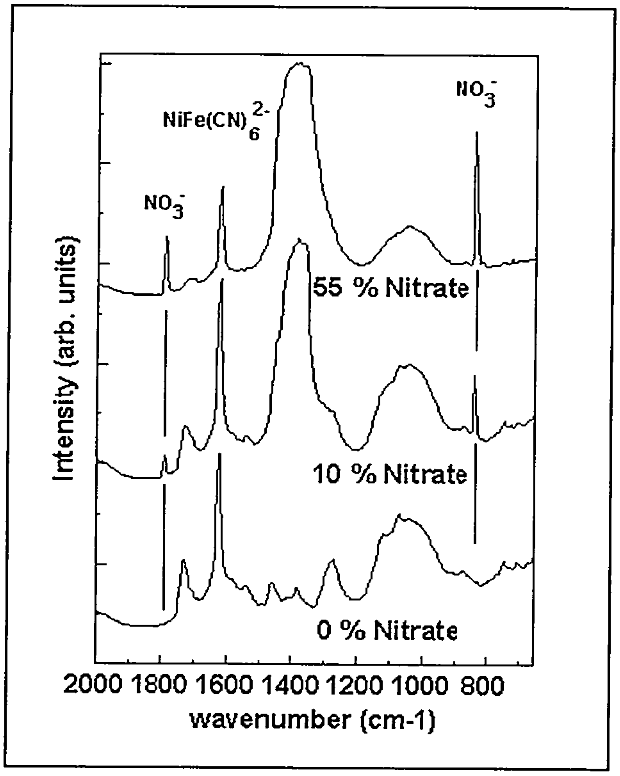

Figure 1.14b. Fourier-transform infrared photoacoustic spectroscopy spectra of three sludge surrogates containing differing amounts of nitrate.

ACCOMPLISHMENTS

FTIR-PAS is a widely used technique for analyzing normally intractable samples. A protocol has been worked out for acquiring reproducible spectra that can be reliably used for quantitative analysis. This includes freeze drying the material, which makes the water content reproducible and, more importantly, prevents migration of soluble components, which occurs during air drying. The migration problem had not previously been recognized by others working on tank material analysis. Figure 1.14b shows example spectra of sludges containing various known amounts of nitrate [NO$_3^-$]. The sharp peaks at 1790 and 840 cm^{-1}, as well as the broad feature at 1400 cm^{-1} and other small features are due to nitrate. The sharp peaks can be used to determine the amount of nitrate in a sample as exemplified by Figure 1.14c. It shows a typical correlation between peak sizes and the amount of nitrate present. Similar features exist for other important components, such as the sharp 1640 cm^{-1} peak for nickel ferrocyanide [NiFe(CN)$_6^{2}$] visible in Figure 1.14b. The first training session for transferring the technology to Hanford is scheduled for March.

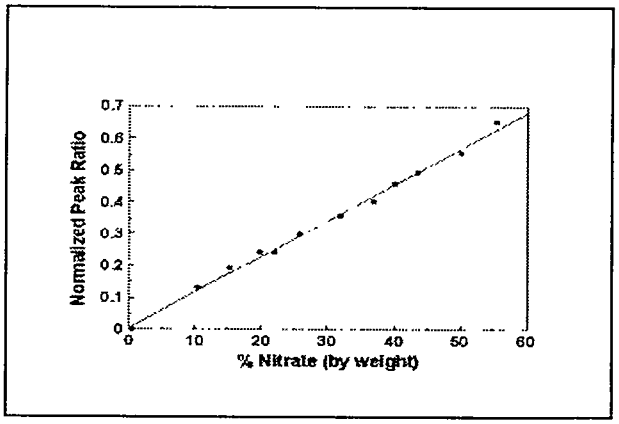

Figure 1.14c. Typical correlation between nitrate peak heights observed by Fourier-transform infrared photoacoustic spectroscopy and the actual nitrate concentration in the sample.

The approach for using TIRS as a monitor for a molten polyethylene/salt stream has been developed. Figure 1.14c shows the excellent correlation between TIRS data and stream composition. Optimization for specific processing-line conditions is underway. A proof-of-principle test has already been carried out at Brookhaven. The TIRS unit will be demonstrated as part of the pilot-scale test of polymer encapsulation planned for later this year at Brookhaven. At the request of Rocky Flats staff, both cold and hot demonstrations of TIRS on the laboratory scale are planned for that location.

COLLABORATION/TECHNOLOGY TRANSFER

Training sessions at Hanford are planned explicitly to transfer the technology to that site. Ames Laboratory has been collaborating with Hanford Site on relevant matters, such as equipment specifications. The photoacoustic detectors used in FTIR-PAS have been commercialized by MTEC Photoacoustics, Inc.. MTEC is the principal producer of photoacoustic detectors worldwide. An MTEC detector was selected for an IR 100 Award in 1985. The project staff has extensive experience assisting end users in applying photoacoustic technology.

The application of TIRS as a waste-process monitor is closely tied to the development of polymer encapsulation occurring at other sites, as shown by the demonstrations discussed in the Accomplishments section. TIRS has also been successfully demonstrated as an on-line process monitor on the pilot and production lines of several manufacturers. It has been demonstrated in the laboratory for a wide range of solid and viscous liquid process stream properties, including chemical composition, cure level of paints and thermoset plastics, and oxidation level and mineral content of coal. The project principal investigators invented TIRS. Iowa State University has patented it, and it is available for licensing. TIRS received a 1992 R&D 100 Award.

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1.15 DEVELOPMENT OF A CONTINUOUS EMISSION MONITOR FOR INCINERATION

TASK DESCRIPTION

This project addresses the need mandated by the Clean Air Act of 1990 to monitor air toxins. The objective is to develop a FTIR spectrometer combined with a heated long-path cell as a continuous emission monitor. The instrumentation will continuously monitor organic and selected inorganic stack emissions. The technology is applicable to incinerators, thermal treatment processes, and ambient air monitoring.

The primary benefit of an on-stream monitor for incinerator effluent is the near real-time determination of incinerator performance. On-stream analysis of the incinerator effluent would satisfy the requirements of the Clean Air Act of 1990 and address public concern about incinerator safety. Other benefits include elimination of the need for a trial burn and the expensive monitoring techniques currently used to characterize the effluent, such as VOST and MM5 sampling trains followed by GC/MS laboratory analysis. These methods are required under current procedures and provide a onetime analysis. Using these methods, monitoring is done only once every 18 months.

In the first year of this project, a laboratory incinerator and an FTIR spectrometer were assembled and tested. The lab incinerator was necessary so that closely controlled and reproducible incinerator conditions can be used to test the precision of the method. FTIR technology was advanced in four areas:

- testing cell materials for stability to hydrogen chloride;
- characterization of flue gas products of incomplete combustion;
- interpretation and evaluation of data quality; and
- development of automated analysis software.

In the second year, a field instrument was constructed and tested at the Toxic Substances Control Act (TSCA) incinerator at K-25 in Oak Ridge, Tennessee. Figure 1.15a shows the field test site. Supporting data analysis and testing were performed using the laboratory incinerator. Data analysis was initiated and advanced algorithms were tested.

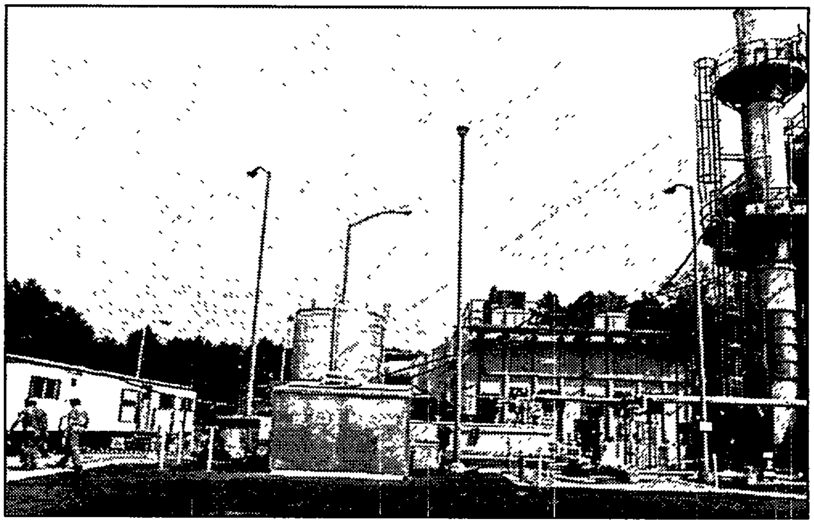

Figure 1.15a. The Toxic Substances Control Act Incinerator at K-25, Oak Ridge, Tennessee.

The EPA has issued a protocol for an FTIR continuous emission monitor. This protocol was adapted into a standard operating procedure that was tested at K-25. The objective is to meet all performance specifications required by the EPA so that the data will be considered compliant.

New data analysis methods are being developed to improve identification and detection levels. Multiple coprocessing of a single spectrum has improved quantitation by reducing noise. Time domain data analysis will also be initiated in combination with spectral analysis. This combined approach will enhance the ability to detect substances that have overlapping absorbances and allow for digital filtering of system noise.

During this year, the commercial instrument will be constructed and tested. A data package will be presented to the EPA as the first step for acceptance of this method. Advanced data analysis algorithms will be pursued and a combined time and spectral domain data analysis method will be field tested at K-25. Copies of the first field test report will be available upon request. An example of the ability of the FTIR monitor to detect emissions is shown in Figure 1.15b, where methane was detected in a single sample. The spectrum illustrated at the top is that of stack gas containing no methane. The middle spectrum shows the presence of methane in the stack sample. The library spectrum of methane is shown in the bottom spectrum.

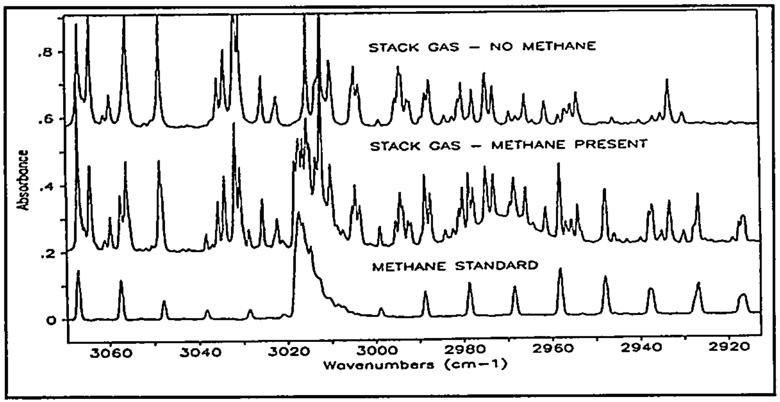

Figure 1.15b. Comparison of stack gas samples with and without methane present.

TECHNOLOGY NEEDS

Title 3 of the Clean Air Act requires monitoring of air toxins from incinerators, stacks and fugitive emissions. This technology is applicable for these requirements and will result in EPA acceptance for FTIR monitoring data. The method can be extended to cover thermal treatment, stack, and ambient air monitoring. Continuous monitoring will directly address issues of environmental safety, and the technology can be used to identify and quantify organic chemicals in the air. There is significant public concern about incineration. A continuous emission monitor addresses those concerns.

ACCOMPLISHMENTS

A laboratory incinerator has been constructed and integrated with an FTIR system. The operating conditions can be deliberately and reproducibly changed to simulate off-set conditions of an incinerator. Data obtained with this incinerator was used in the design of the prototype instrument. After laboratory testing was completed, the prototype instrument was field tested at the K-25 mixed waste (TSCA) incinerator at Oak Ridge. The initial testing was undertaken to ensure the technique will be EPA-compliant and follows the requirements of the EPA Protocol. EPA Performance Specifications Testing is in progress.

There have been significant advances in instrument design. The optics have been redesigned so the instrument can be moved easily and set up without disturbing optical alignment. The commercial instrument will consist of three modules that can be snapped together.

Data analysis will be much more sophisticated than found in conventional instruments. Data will be analyzed in both the time and spectral domains. Extensive use of coprocessors will provide rapid results and dramatically reduce the problem of spectral interferences. Digital filtering of the data will enhance detection levels.

COLLABORATION/TECHNOLOGY TRANSFER

A CRADA is currently under development with Clean Air Engineering (CAE) to advance the commercialization of the system. CAE will assist in testing the instrumentation and in developing stack sampling technology that is appropriate for this new technology.

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1.16 HYDRAULIC AND DIFFUSION BARRIERS IN THE VADOSE ZONE SURROUNDING BURIED WASTE

TASK DESCRIPTION

This investigation will develop and test new barrier materials specifically for buried waste control. (see Figure 1.16). Tests will determine the long-term durability of the material, permeability to groundwater, ionic diffusivity, response to wet/dry cycling, and chemical resistance to acid, base, and organic solvent conditions that might occur at waste sites.

This study will also examine the effects of aggregate type and quantity on barrier performance. Inert aggregate substances such as clean sand and recycled glass used to produce the test specimens will be optimized to binder, geological, environmental and waste conditions.

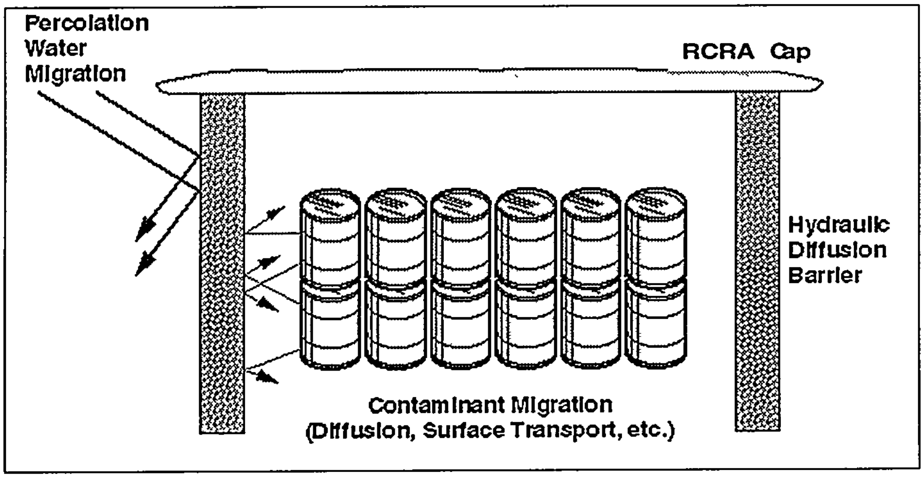

Figure 1.16. Reduction of contaminant migration and mobility using hydraulic/diffusion barriers.

Because the investigation will examine new applications of barrier constituents, regulatory issues affecting approval of barrier construction have been surveyed. This survey was a general overview of the regulatory concerns for emplacement of polymers and binders in soils, and included a specific focus on the use of thermoset resins.

TECHNOLOGY NEEDS

Sites with components that are not controllable with contaminant-specific sorbents will require barriers that prevent the movement of contaminated groundwater. Systems that use direct injection of barrier reagents as liquids, and subsequent in situ formation of the barrier, are preferred over those involving excavation.

Currently approved clay-based barriers may not be as effective as some synthetic polymers and resins. These agents may cement and seal sediments to form impermeable, chemically-resistant barriers to water movement. In some situations where in situ formation is not possible, and excavation costs are not prohibitive, barriers constructed with synthetic binders and an inert matrix provide an alternative. This investigation includes the search for appropriate matrix aggregates.

ACCOMPLISHMENTS

- The report, "Regulatory Issues and Assumptions Associated with Barriers in the Vadose Zone Surrounding Buried Waste", was issued.
- Inert barrier aggregate mixes of sand, sand and stone, and sand and recycled glass were selected.
- Binders and resins chosen included vinyl ester styrene, polyester styrene, polyacrylate, a furfuryl polymer, and petroleum bitumen.
- Over 1000 test samples were evaluated for compatibility and engineering performance; testing has been initiated.

COLLABORATION/TECHNOLOGY TRANSFER

All work on this project is currently being accomplished through the facilities of the Brookhaven National Laboratory's (BNL) Waste Management Group. Because one of the planned aggregate mixes involves recycled consumer glass waste, some cooperation with a municipal or commercial recycled glass supplier is envisioned.

Communication of the results of this investigation will be through an expert review panel workshop. Attendees will include BNL, DOE, and industry personnel. A summary report will be issued containing workshop results. Further technology transfer will include dissemination of study results at symposia and meetings of professional and industrial associations.

Potential demonstration sites are through the Buried Waste Integrated Demonstration, the Mixed Waste Landfill Integrated Demonstration, and the Underground Storage Tank Integrated Demonstration. Discussions at the Brookhaven Waste Management Group are identifying when and how the results of this investigation will be used.

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1.17 IN SITU GROUNDWATER TREATMENT USING MAGNETIC SEPARATION

TASK DESCRIPTION

This project will implement and demonstrate Bradtec's MAG*SEP™ technology for in situ groundwater treatment. The MAG*SEP™ technology uses specially designed particles to selectively adsorb contaminants from effluent water or groundwater. The technology can recover low levels of radioactive and/or inorganic hazardous contamination (in the ppb range) while leaving non-radioactive non-hazardous species unaffected.

The selective adsorption particles are composites manufactured in one of two forms. The particles can range in size from 1 to 15 microns, have a magnetic core, a polymer coating for durability, and either a "functionalized" resin coating or selective seed materials embedded in the polymer coating.

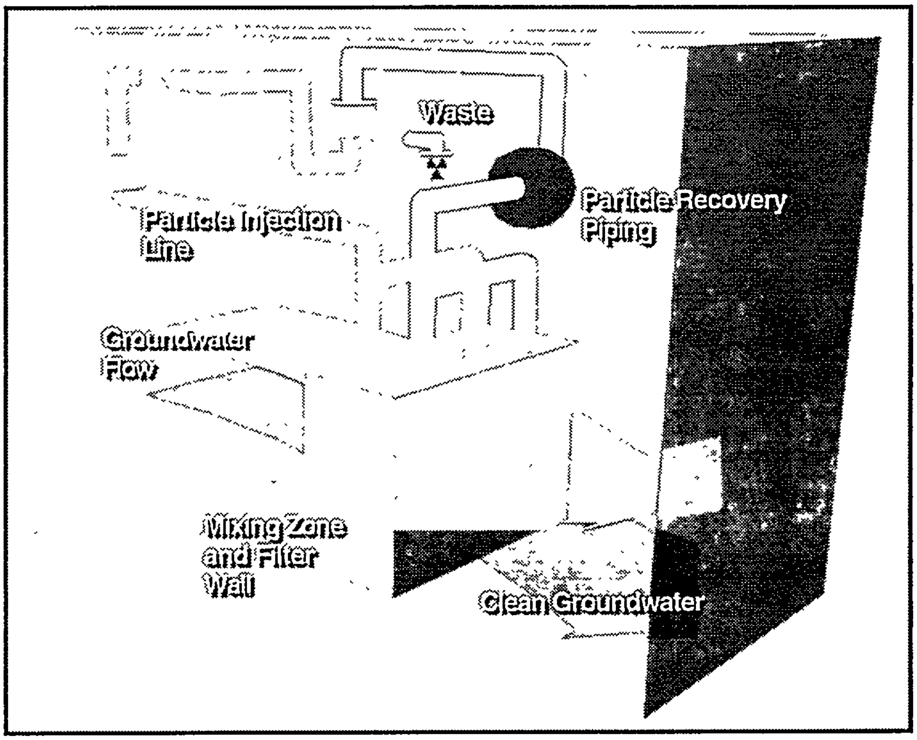

Figure 1.17. MAG*SEP™ Groundwater Treatment.

In treating contaminated water, the particles are injected into the water where they adsorb the contamination. Because the particles are small, and adsorption is a surface phenomenon only, the adsorption kinetics are very rapid (typically less than one minute). The particles are then recovered from the water using a magnetic filter. The magnetic core gives the particle a very high magnetic susceptibility. Also, because the contamination is chemically bound to the particles, adsorbing non-magnetic contaminants can be removed from water with high decontamination factors. Once the particles have been recovered on the magnetic filter, the filter is backwashed, the particles regenerated (much in the same manner as ion exchange resin is regenerated), the contaminants recovered (for recycle or treatment), and the particles reused.

The technology can be applied in situ for the recovery of radionuclides, heavy metals, and nitrates from groundwater. For in situ treatment, a "filter wall" is installed to prevent the groundwater from moving beyond the filter wall, except by passing through it. There are two zones in the filter wall: first, a mixing zone where MAG*SEP™ particles are injected and mixed with the water, and second, the magnetic recovery zone. The collected particles are then pumped to the surface for regeneration and reuse. Figure 1.17 depicts the in situ MAG*SEP™ groundwater treatment process.

The specific tasks within this project include a pilot-scale proof of concept test that evaluates the process chemistry and specific adsorption of contaminants from water obtained from DOE sites. Adsorption kinetics, effects of competing ions, and organic/humic interferences will be evaluated along with decontamination factors and MAG*SEP™ particle regeneration.

TECHNOLOGY NEEDS

The magnetic filters and other equipment are all commercially available. Magnetic filtration, in fact, is an established technology used in water treatment for boilers and for removing iron contamination from pulp in paper manufacture. In boiler feed treatment, the iron present in water is removed by magnetic filtration. Other contaminants which are paramagnetic can also be removed. An example is copper. However, because there is no chemical bond between the iron and copper, the iron is typically removed with a decontamination factor between 20 and 100, while the decontamination factor for copper is typically 2 to 3.

The new feature of this technology is the development of the composite particles. With the MAG*SEP™ process, paramagnetics are not utilized, and the ability to recover the MAG*SEP™ particles with the contaminant is equal to the ability to recover iron which is well established with magnetic filters. No other processes use chemical treatment to prepare particles which can selectively adsorb contaminants onto a magnetic particle with a high magnetic susceptibility. To apply the MAG*SEP™ technology in situ, a means to inject and mix the MAG*SEP™ particles with contaminated groundwater, recover the MAG*SEP™ particles, and transfer the MAG*SEP™ particles to a regeneration/recovery system must be developed and demonstrated.

ACCOMPLISHMENTS

Tests conducted at Chemical Waste Management's Clemson Technical Center have removed 100 percent of the MAG*SEP™ particles in a liquid stream.

COLLABORATION/TECHNOLOGY TRANSFER

Bradtec has exclusively licensed this technology to Chemical Waste Management, Inc., for application in North America. Bradtec has purchased a pilot-scale Electromagnetic Filter from Babcock and Wilcox Nuclear Technologies. Two test sites (Berkeley Pit and Savannah River Site) have been selected for pilot scale demonstrations.

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1.18 EQUIPMENT DEVELOPMENT

TASK DESCRIPTION

The focus of this study area is on the vitrification and associated supporting equipment to be used in the Minimum Additive Waste Stabilization (MAWS) concept, with a view toward the feasibility of producing an *environmentally-sound and durable final waste form.* The objective is to assess the current state of vitrification technology and choose those technologies for further radioactive waste treatment development that have a proven record of accomplishment, reliability, and commercialization in the private sector. Once these assessments have been completed, a long-range plan needs to be developed that will provide costs and strategies to bring these technologies on-line for radioactive waste treatment. It is initially envisioned to assess two technologies at the bench-scale, and then choose one for further development at the pilot-stage. A plasma technology has been identified as one likely melter configuration which is now being assessed at the bench-scale.

The comprehensive plan to implement/coordinate additional MAWS developmental work needed for equipment evaluation was prepared and completed in 1993 by MSE, Inc. with guidance from DOE. MSE is identifying potential entities (industries, academia, and the National Laboratories) for their specific expertise to conduct work in the following technology areas:

- Materials science studies to determine the matrix of test materials.
- Identification and assessment of promising technologies as to MAWS applicability, their maturity stage, and availability of equipment for testing. This includes recommendation of a few of the most promising technologies for further development.
- Identification of testing facilities (rad/non-rad) for capabilities.
- Waste product long-term durability testing to validate the waste form quality.
- Preliminary life cycle cost estimation.
- Cost and overall schedule for the entire package.

MSE will solicit input from appropriate entities to participate in various parts of the MAWS concept, review their proposals, and make recommendations in the area of promising equipment to be developed. MSE will integrate the recommended proposals and propose an overall plan and schedule to initiate work in late FY94.

Work to this point has focused almost entirely on a low temperature joule heated melter system. In other variations of vitrification technology, a plasma or microwave system may be employed as a high temperature process operating between 1800 to 2600°C. In such a system a more viscous glass or slag can be produced with fewer limitations on metals content or organics in the waste streams chosen. As before, the cost-effectiveness of the technology compared to other technologies will be the main driver along with production of a stable, durable final waste form.

Initial evaluation tests are currently underway using the Plasma Centrifugal Furnace (PCF) technology available from Retech, Inc. These tests are being coordinated by MSE, Inc. In these tests, metal loadings up to 70 % are anticipated which will produce a durable final slag waste form. Produced wastes will be carefully evaluated by Toxicity Characteristic Leach Procedure tests, metal loadings up to 70 percent are anticipated which will produce a durable final slag waste form. Produced wastes will be carefully evaluated by Toxicity Characteristic Leach Procedure (TCLP) and Product Consistency Test (PCT) determinations. In addition, off-gas data will be collected and assessed to determine the effectiveness of the technology system as a whole for treating waste and posing no further threat to the environment.

Pending the results of the bench-scale testing work and the direction chosen, future development work may be required to begin the scale-up to a commercial size vitrification system which can be incorporated into the overall MAWS concept. This future pilot stage should probably be site specific for a particular set of waste streams that can best use this technology.

TECHNOLOGY NEEDS

To compliment the compositional envelope work, several vitrification technologies need to be evaluated to be able to handle waste streams not suited to the low-temperature joule-heated melter. Much of this development work can be done concurrently with the compositional development work by using a mix of actual and simulated waste streams in test work. The real waste streams will serve to focus the efforts on real problems while the simulated waste streams will allow maximum information to be derived from compositional variation. For easy transfer to the many potential waste sites, assessments as to the maturity of the specific technology need to be done. In many cases, this may require both bench-scale evaluations as well as pilot-plant operations to minimize risks and potential problems when the technology becomes commercial.

It is the desire to practice the MAWS concept with various technologies to fulfill a wide range of treatment needs. Technologies to compliment the current low temperature Joule-heated furnace configuration are needed particularly for wastes with a high metals content. One example of such technology is the plasma centrifugal furnace which needs to be proven in its ability to completely oxidize the metals to arrive at a stable and durable waste form. The results should give an initial indication of the capability of plasma utilizing the MAWS concept.

ACCOMPLISHMENTS

- A low temperature Joule-heated melter has been developed and radioactive feeds tested at the bench-scale. The melter has successfully processed high fluorine wastes to produce quality glasses.

- The procurement package for Retech to do the plasma testing at Ukiah, CA has been completed and approval has been issued to Retech.

- Provisions have been made for off-gas sampling during the tests to provide data on problem volatiles.

- Initial tests have indicated that the equipment is capable of melting mixed high metal containing wastes; complete metal oxidation has been achieved in a test with up to 70 percent carbon/stainless steel. More work is being done to optimize furnace operational parameters and explore compostional variation.

- A draft of the long range plan has been put together which identifies both single and two stage thermal treatment options and fast track versus normal development options.

COLLABORATION/TECHNOLOGY TRANSFER

Current technology development of the PCF is being coordinated through MSE, Inc. at Retech in Ukiah, CA. Laboratory evaluation of waste forms for this work is subcontracted to Argonne National Laboratory. The long range plan for high temperature technologies is being developed by MSE, Inc. with consideration given to conducting the test program at qualified university or industry participants.

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1.19 WASTE FORM DURABILITY/CHARACTERIZATION

TASK DESCRIPTION

All glass and glassy slag forms are not equal, and therefore need to be evaluated as to their long term stability and leach resistance. Wide variation in properties can be achieved depending on the composition, and the specific tests carried out may influence the conclusions. Also, most stability and durability tests are carried out for only relatively short times in comparison to the actual time frame required for safe disposal of the materials produced. For this reason waste form durability and characterization is a major effort of the MAWS program and the main reason that glass/slag waste forms through vitrification were chosen.

An objective of the MAWS program is to provide a framework in which waste streams can be rather quickly screened, classified, and compared to the compositional envelope information already collected, but also to add to this information wherever possible to expand the acceptable regions. This involves extensive durability and leach resistance data which will be collected in a database and modeled where appropriate to reduce the effort required in subsequent searches for an acceptable mix of components. Feeding into this database will be not only compositional data, but also data from tests such as TCLP, PCT, and vapor phase tests. These provide both short and intermediate range results which can be projected to long term scenarios. Specifically the PCT tests may be carried out over 7, 28, 91, 180, and up to 730 day time periods. Such tests carried out at 90 percent relative humidity and 90°C provide an accelerated weathering environment in which new phases may form or surface reactions can occur to alter the stability of the glass/slag waste form.

TECHNOLOGY NEEDS

Once the MAWS concept proves to be technically feasible and economical for a particular set of waste streams, further testing is needed to demonstrate that the vitrified waste product will endure with time and will be protective of the environment. Within the MAWS concept, extensive testing is included to provide a database of the quality, consistency, homogeneity, leachability, and durability of the vitrified waste product. Expected long-term performance of the glass will be determined and documented. These data may then be used to supplement the existing database on glass performance (mainly high-level waste glass) for use in studies to determine whether it is possible to place the treated waste in less expensive disposal facilities (possible delisting), thus further reducing site remediation costs.

A three-tiered leach testing approach for durability will be used:

- Standard toxicity characteristic leaching procedure and product consistency testing for leachable inorganics;
- Service condition testing; and
- Accelerated testing (vapor test) for surface reactions leading to crystal phase formation.

This tiered approach will identify and provide for practical testing methods that can be used to determine the performance of the vitrified product (including elemental and radionuclide release characteristics) under disposal conditions. A variety of other leach testing methods will also be used in conjunction with detailed surface analyses by analytical electron microscopy, scanning electron microscopy, secondary ion mass spectrometry, and optical microscopy. The objective of these tests will be to establish a meaningful testing approach and database for demonstrating the durability of the glass product.

ACCOMPLISHMENTS

- Two regions of relative durability/stability have been identified. The first is a true glass capable of incorporating high flux and fluoride levels, but low metals. The second is a slag form capable of incorporating high metals as oxides, but low fluxes.
- Glasses and slags have been produced that pass TCLP tests, and have PCT and vapor test results equal to or better than Savannah River high-level waste glass standards.

COLLABORATION/TECHNOLOGY TRANSFER

This work is being carried out by the Vitreous State Laboratory of Catholic University of America for glass waste forms and by Argonne National Laboratories for glassy slag waste forms. Compositional model development coordination between both facilities is in progress.

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Application of the MAWS concept may take many forms of integrated systems which will be dependent on the particular waste streams being combined. The particular integrated system chosen for Fernald consists of vitrification, soil washing, and ion exchange/water treatment (See Figure 1.20a).

VITRIFICATION

The Fernald variation of MAWS vitrification technology is directed at lower temperature processes in the range of 1100 to 1600°C. At these elevated temperatures, glass becomes electrically conductive, and the current passing between the electrodes in a vitrifier causes the conductive glass to heat, thereby maintaining the glass in a molten state. This process is known as joule-heating. Most inorganics oxidize and dissolve in the molten glass because the great majority of oxides are soluble in silicate glasses; organics rapidly oxidize at the high temperatures and form simple gases (mostly carbon dioxide and water vapor) that are collected and treated in the off-gas system.

Such a vitrification system (GTS Duratek Duramelter™) capable of producing at least 100 kg/d of vitrified waste from radioactive feed materials is located at the Vitreous State Laboratory of Catholic University of America. This system will provide critical large-scale process data necessary for the development of process controls and operating protocols for the 300-kg/d system installed at FEMP. Process data will include throughput rates, cold cap formation, and information on foaming events, as well as off-gas system performance evaluation. Additionally, supporting data for scale-up to the larger pilot-scale and full-size units will continue to be collected from 10-kg/d and 100-

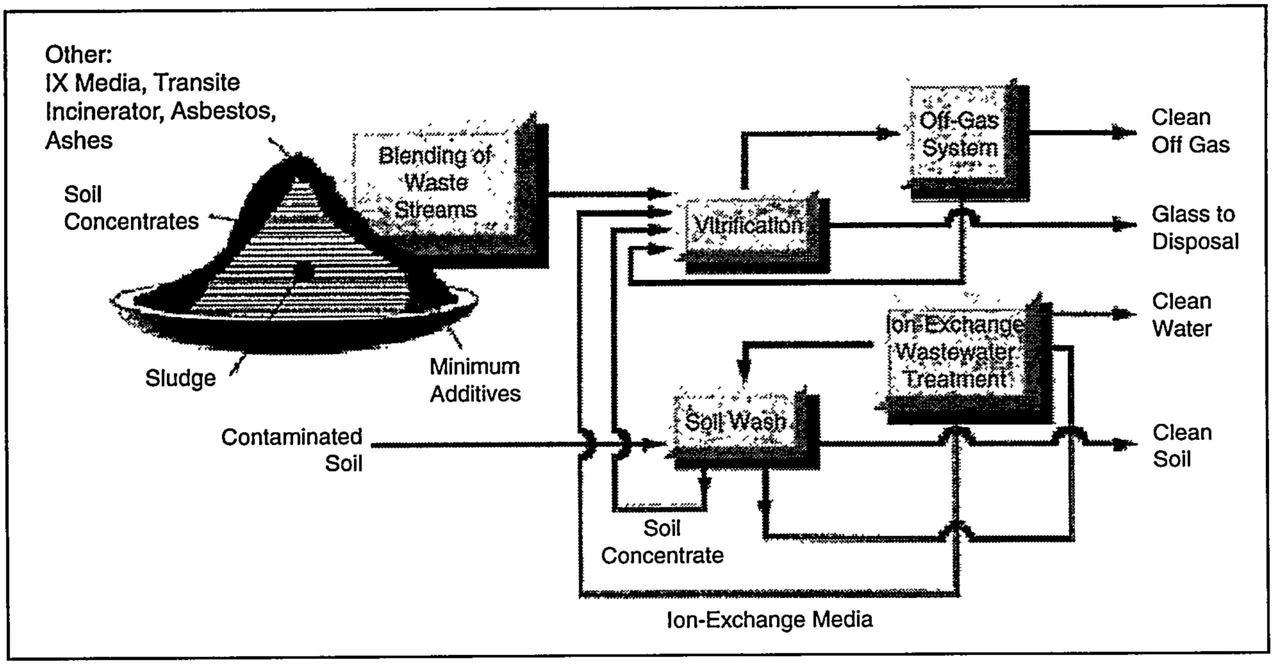

Figure 1.20a. The MAWS Technology System.

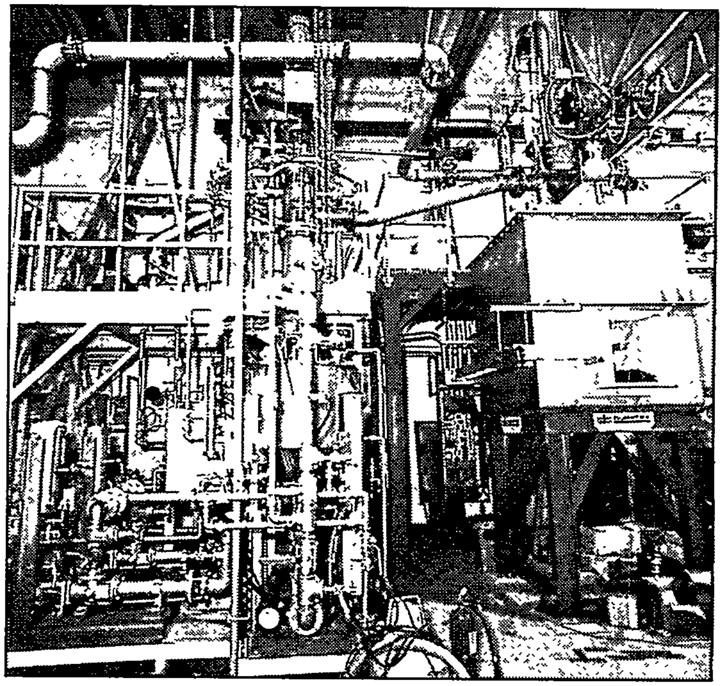

Figure 1.20b. The FEMP Vitrification and Off-gas System.

kg/d units in conjunction with the 300-kg/d system to be used for the demonstration.The vitrification system to be demonstrated at FEMP will produce 300 kg/d of glass from radioactive waste. An extensive on-site testing program will be conducted to provide the essential system performance and operating data necessary for treatment technology selection at FEMP. These data will also provide the basis for scale-up to larger pilot-scale and full-scale treatment systems. The FEMP vitrification system has been designed to handle a blend of pit sludges, spent resins, and soil concentrates (See Figure1.20b). This MAWS system will be capable of dispensing the vitrified product into drums in the form of glass gems. The gems will be of various sizes to facilitate packing and enhance volume reduction while maintaining easy handling of the vitrified product.

The off-gas system will have an advanced two-stage caustic scrubbing system designed to produce no secondary waste streams. The off-gases will then be treated by high-efficiency particulate air (HEPA) filtration to meet regulatory requirements for release. Produced sludges will be recycled to the melter. Monitoring equipment will also be provided.

SOIL WASHING

Soils, primarily contaminated with radioactive constituents, will be washed with the TRUclean™ process to separate them into clean soils and soil concentrates. This will be accomplished by passing a slurry of the contaminated soils through a seriesof scrubbers, gravimetric separators, and hydrocyclone separators. Laboratory studies of FEMP soils have been performed to specify the demonstration unit, and a carbonate leach step has been added to achieve the target uranium cleanup level. The demonstration unit at FEMP is able to process 0.25 yd^3/h of soil (see Figure 1.20c). The soil concentrates will be used as feed for the vitrification system. All

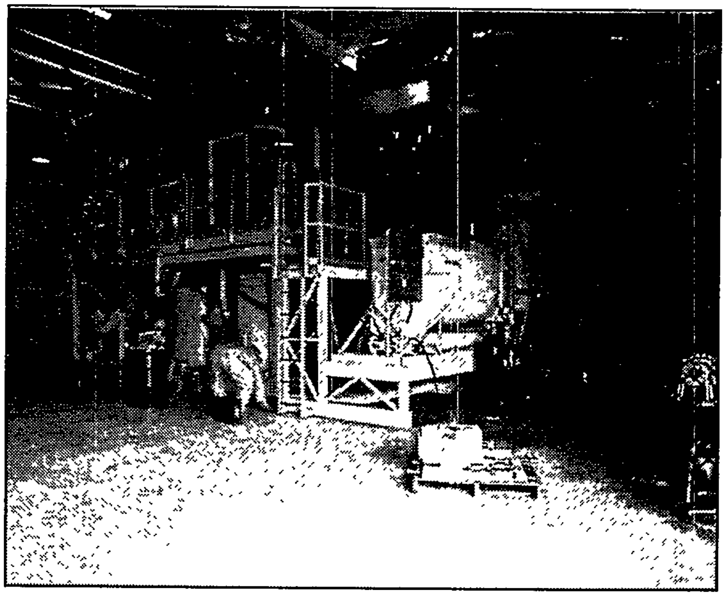

Figure 1.20c. The FEMP Soil Washing System.

input and output streams will be analyzed for contaminants to determine the success of the soil washing for radionuclide removal and other RCRA contaminants, if appropriate. Mass balance calculations will verify final disposition of the contaminants. These studies are being conducted in close collaboration with the laboratory water treatment studies to ensure that the effluent from the process can be treated in the ion-exchange system and then recycled to the melter for ultimate stabilization of the contaminants in the vitrified glass product.

ION EXCHANGE WATER TREATMENT

The water treatment system will treat contaminated wastewater from the soil washing systems. Uranium and thorium contaminants will be stripped off by a traditional organic ion-exchange resin and redeposited onto a glass resin that can be fed to the vitrifier, allowing for conventional disposal of the spent organic resin. The success and economics of this process will be evaluated and documented at the end of the FEMP demonstration. If necessary, the process can be modified to remove hazardous constituents, such as toxic metals, to ensure that all water quality standards are met for water discharged from the system. An acid-stripping process will be developed for regenerating the Dowex 21K organic ion-exchange resin used in the water treatment system. The stripped uranium will then be collected and used as feed for the melter.

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Waste Retrieval and Processing

Section 2.0

2.0 WASTE RETRIEVAL AND PROCESSING OVERVIEW

Waste retrieval and processing constitutes one of the largest DOE problems. Within the DOE Complex, large quantities of high-level waste, low-level waste, and transuranic waste have been buried or stored and need retrieval and treatment. Before 1970, most low-level and transuranic wastes were buried in common shallow land burial grounds. A majority of the high-level waste was stored in underground storage tanks.

DOE has identified more than 1 million 55-gallon drums and boxes of waste in storage, and 3 million m^3 of buried waste. Over the years, many of the older disposal containers have been breached, resulting in contamination of the adjacent soil. Considering transuranic solid waste, approximately 190,000 m^3 have been buried, and 60,600 m^3 have been retrieved and stored. Mixed transuranic waste composes 58,000 m^3 of this inventory. High-level waste stored at four DOE sites represent another 381,000 m^3 of volume. Of this, 77 million gallons of high-level waste are contained in 332 underground storage tanks as sludge/liquids and approximately 4,000 m^3 are stored as granular calcined solids. Since most of the high-level waste is mixed with hazardous contaminants, it is considered mixed waste. The remainder of the stored waste, about 3,000,000 m^3, is low-level waste and includes 247,000 m^3 of mixed low-level waste. No effective treatment is known for 107,000 m^3 of this mixed low-level waste.

Effective May 8, 1992, all DOE mixed-waste streams fell under EPA's land disposal restrictions and, as such, can no longer be disposed of without prior treatment to destroy, separate, or immobilize the hazardous component. All mixed low-level and high-level waste must be treated before final disposal. In the case of mixed transuranic wastes destined for deep geologic disposal, the hazardous components must not exceed established waste acceptance criteria. Most of the hazardous components of the mixed wastes have not been characterized; however, from past knowledge, they represent the entire gamut of organic and inorganic hazardous wastes. Available technology is inadequate to solve many of the problems at hand.

Another form of waste, representing potentially large volumes, is associated with decontamination and decommissioning of contaminated buildings and equipment. More than 500 separate facilities have been identified, and it is possible that as many as 7,000 facilities at 39 different sites could be scheduled for decontamination and decommissioning. Although materials will be recycled when possible, this activity will result in new waste generation that is immeasurable at this time. Additionally, as much as 20,000 m^3 of mixed waste, in 100 separate waste streams, is still being generated on an annual basis from ongoing facility deactivation and transition activities.

Developing cost-effective innovative hazardous and mixed waste characterization and treatment technologies is not only a requirement for DOE, but for other Federal agencies and commercial businesses. EPA estimates a total present value cost of about $18.7 billion, and an annual cost of about $1.8 billion using available technologies. Furthermore, EPA assumes there exists approximately 773,000 sites with underground storage tanks that are subject to regulation and remediation.[2] Most of these tanks contain petroleum products and require remediation of the tank as well as the surrounding soil as a result of leakage problems. Although occurrences of radioactive contaminated waste is less frequent in the public sector, there are no widely accepted technologies available to treat this waste. Development of efficient, low-risk mixed waste treatment systems and facilities is one of the most pressing issues facing public and private environmental restoration and waste management efforts.

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[2] U.S. Environmental Protection Agency, Office of Policy, Planning and Evaluation, Environment Investment: The Cost of a Clean Environment, EPA-230-11-90-083, November 1990.

2.1 POLYETHYLENE ENCAPSULATION OF LOW-LEVEL WASTE

TASK DESCRIPTION

The initial objective of this project under development at Brookhaven National Laboratory is to investigate the effects of high radiation doses and elevated temperatures on polyethylene mechanical and leaching properties. Polyethylene is an inert thermoplastic polymer with a processing temperature of about 150°C. The polyethylene is produced using a screw extrusion process, which simultaneously heats, mixes, and conveys the waste and binder (see Figure 2.1). A homogeneous, molten mixture is extruded into a container for cooling. Once this mixture is cooled below 120°C, a monolithic waste form is ensured. Upcoming tests include treatability studies using surrogate Hanford waste to examine waste loading potential and waste form performance. Ultimately, full-scale technology feasibility will be demonstrated.

TECHNOLOGY NEEDS

Polyethylene encapsulation is a waste form developed to treat mixed tank waste separated from the sodium-nitrate high-level waste present at many DOE facilities (Hanford, Rocky Flats, Savannah River, Oak Ridge, and West Valley). This demonstration is driven by the Hanford Federal Facility Compliance Agreement (FFCA), which mandates identification of tank waste disposal methods by 1999 and full-scale single-shell tank (SST) closure by 2004. Completion of the cited tasks by the end of 1995 is needed in order to evaluate the applicability of polyethylene encapsulation for SST low-level waste treatment/disposal and to provide necessary data for comparison with the base-line technology, grout solidification, on time to meet the FFCA scheduling milestones.

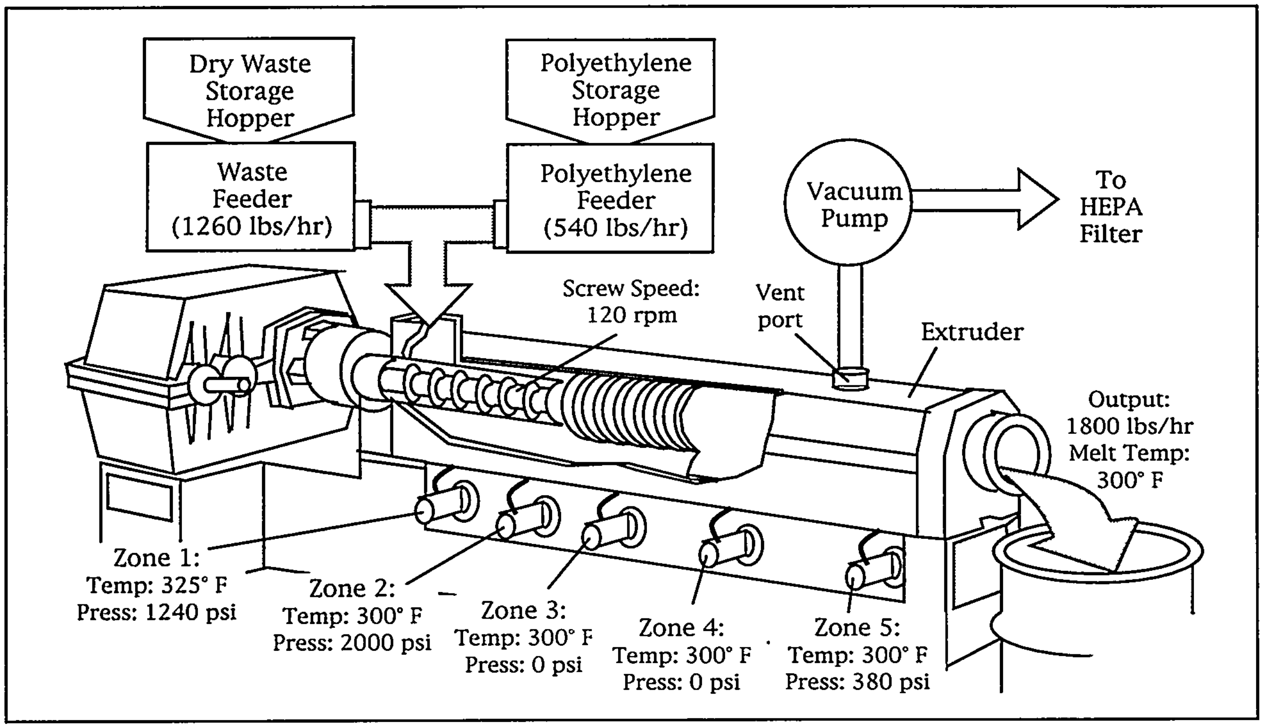

Figure 2.1. Polyethylene Encapsulation System.

Polyethylene waste forms are superior to grout waste forms. Polyethylene is less dependent on the waste chemistry, accepts a wider range of waste types, and increases waste loading. Finally, polyethylene is easier to process under heterogeneous waste conditions.

ACCOMPLISHMENTS

Extensive waste form performance testing has been completed, including compressive strength, water immersion, thermal cycling, radioactive and hazardous constituent leachability, radiation stability and biodegradation. Scale-up feasibility has been confirmed by processing simulated nitrate wastes at production output rates up to 2,000 lbs/hr.

For nitrate salt wastes, polyethylene encapsulation provides between 3.5 and 5 times greater volume reduction than conventional cement-based grout formulations. Microencapsulation of individual contaminant particles results in leachabilities measured at 100 to 1000 times lower than grout waste forms. Waste forms containing up to several hundred ppms of toxic metal contaminants have passed the Environmental Protection Agency's Toxicity Characteristic Leaching Procedure.

COLLABORATION/TECHNOLOGY TRANSFER

As of February 1993, a waste management vendor was negotiating a Cooperative Research & Development Agreement with BNL for the application of polyethylene encapsulation to utilize this technology for improved waste treatment at DOE and commercial nuclear waste generation sites. A patent application is being prepared for submission.

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2.2 TRUEX MODEL DEVELOPMENT

TASK DESCRIPTION

The TRUEX process is a solvent extraction procedure that can very efficiently separate transuranic (TRU) elements (e.g., Np, Pu, Am and Cm) from aqueous nitrate- or chloride-containing wastes. These wastes are typically generated in reprocessing plant operations or in plutonium production and purification operations. The resulting solutions after extraction may be sufficiently free of TRU elements to warrant their disposal as non-TRU, low-level wastes. Furthermore, plutonium can be recovered and purified by this process. Treatment of stored wastes by the TRUEX process will lower the costs of final disposal significantly; treatment of waste streams as they are generated will allow recycle of streams and avoidance of future waste treatment and disposal costs.

The key extractant in the TRUEX process is octyl-(phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide (CMPO) (see Figures 2.2a and 2.2b). It is combined with tributyl phosphate (TBP) and a diluent to formulate the TRUEX solvent. The diluent is typically a normal paraffinic hydrocarbon (either a C_{12}-C_{14} mixture or n-dodecane) or a non-flammable chlorocarbon such as tetrachloroethylene.

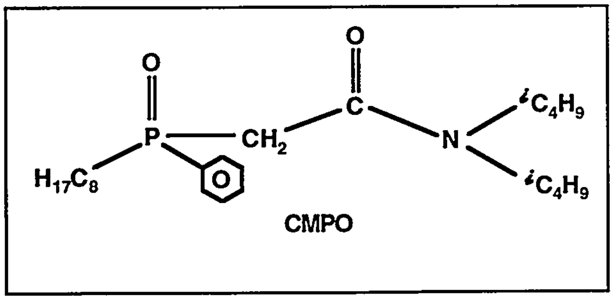

Figure 2.2a. CMPO-Extractant Chemical Formula.

The Center for TRUEX Technology Development at Argonne National Laboratory (ANL) continually performs research and development (R&D) to broaden the applicability of the TRUEX process in the treatment of high-level waste and TRU-containing waste streams. A major part of the effort was to develop and upgrade the Generic TRUEX Model (GTM) to assist in designing feed- and site-specific processes and evaluating their economics. The GTM is an user-friendly computer software that models and predicts the TRUEX extraction behavior, calculates TRUEX flowsheets, and estimates space and cost requirements for installation. The GTM runs on a personal computer (IBM-compatible or Macintosh), and is executed by Microsoft Excel software.

$$Am^{3+} + 3NO^-_3 + 3CMPO \longrightarrow Am(NO_3)_3\,(CMPO)_3$$

Aqueous Phase **Organic Phase** **Organic Phase**

Figure 2.2b. TRUEX-Process Extraction Equilibrium Example.

The objective of the current task is to validate and refine the GTM's ability to design flowsheets for specific feeds and process goals and to predict extraction behavior of feed components and potential processing difficulties. This task also aims to discover and identify R&D needs for getting TRUEX ready for broader implementation. The TRUEX processing of actual HLW and TRU wastes at Oak Ridge National Laboratory (ORNL) will validate the GTM. Finally, ANL will cooperate with the Power Reactor and Nuclear Fuel Development Corporation (PNC) of Japan to model their data on continuous TRUEX processing of high-level waste.

TECHNOLOGY NEEDS

If the TRU content of TRU waste streams can be lowered to below 100 nCi/g of solid, the waste can be classified as non-TRU. Additionally, if the radioactivity of other isotopes, such as ^{137}Cs and ^{90}Sr, is reduced to an acceptable level, the wastes will be eligible for near-surface disposal. Use of the TRUEX process to treat TRU waste will greatly reduce the volume of high-level waste, resulting in high cost savings during disposal.

The GTM is an indispensable tool in designing site- and feed-specific TRUEX flowsheets and estimating the space and cost requirements for a TRUEX process installation. The continuous enhancement of the GTM through improved thermodynamic and computer modelling will require a parallel validation of the model by collecting laboratory and pilot-plant data.

ACCOMPLISHMENTS

Modifications to the GTM have been completed to allow design of a TRUEX processing flowsheet for Mark 42 targets (ORNL). Test runs using the Mark 42 dissolution feed material have also been concluded. Data collection for zirconium and fluoride has been completed, while that for chromium and thorium has begun. Version 2.7 of the GTM has been completed, tested, and released.

COLLABORATION/TECHNOLOGY TRANSFER

All technical users at ANL, Hanford, Idaho, Los Alamos, ORNL and Rocky Flats share information pertaining to further development and use of the model. University partners at the University of Illinois and Spring Arbor College, MI are collecting extraction data. Collaboration also exists to demonstrate the process and model the data with the PNC of Japan.

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2.3 MAGNETICALLY-ASSISTED CHEMICAL SEPARATIONS

TASK DESCRIPTION

This work will explore a process combining the selective and efficient separation afforded by chemical sorption with the magnetic recovery of ferromagnetic beads. The objective is to develop a compact, economic, in-tank or near-tank process for the removal of contaminants such as Cs, Sr, and TRUs from aqueous wastes stored at DOE sites. The magnetically-assisted chemical separation (MACS) uses magnetic beads coated with either a selective ion-exchange material, an organic complexant containing a solvent for contaminant removal, or solvents for the selective separation of TRUs (see Figure 2.3). The beads are formed from a magnetic material coated with organic polymer or bonded ion-exchange resin. Organic solvents can be adsorbed onto the polymeric surface by contacting the beads with a solution of the solvent in a volatile diluent. The coatings extract the contaminants and the beads are then magnetically removed. The beads can either be directly added to the vitrification slurry, or the contaminant can be removed by a stripping procedure to regenerate the extracting beads.

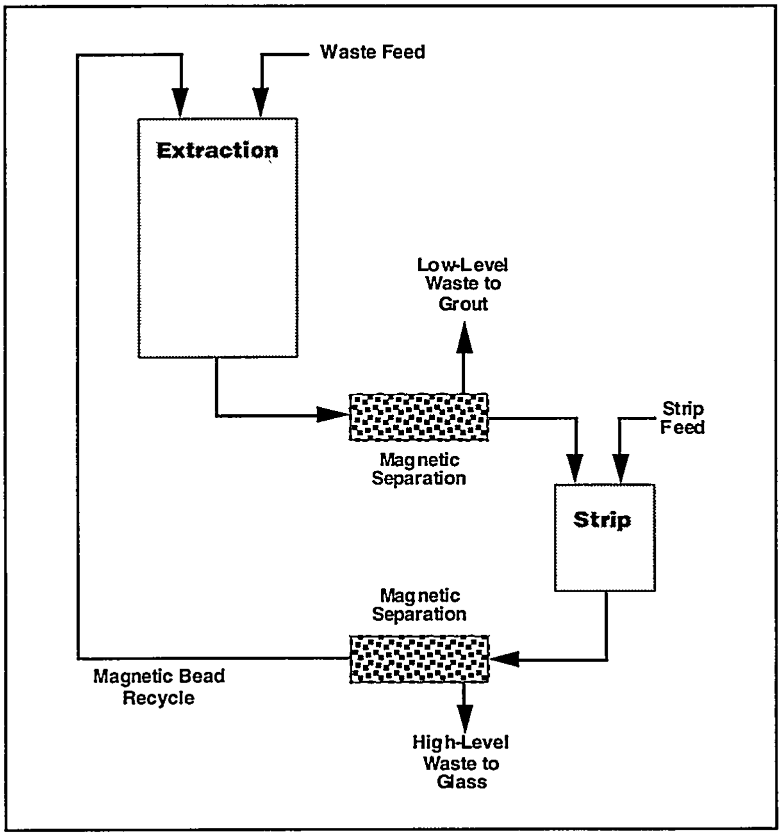

Figure 2.3 The Magnetically-Assisted Chemical Separation Process.

TECHNOLOGY NEEDS

The removal of Cs, Sr, and TRUs is important for the safe and economic disposal of Hanford tank wastes and other DOE waste streams. The problem is complicated by the need for the separation to be achieved using compact and economic in-tank or near-tank processes that produce small secondary waste streams. The promise of this work is that these criteria can be addressed by a process that also has the flexibility to be adapted to the removal of other contaminants.

ACCOMPLISHMENTS

Magnetic particles coated with several compositions of octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide/tributyl phosphate (CMPO/TBP) mixtures have been prepared; optimization of the coating composition and coating process continues. In tests of the ability of these substrate-coated particles to remove americium from 2 molar nitric acid, a reduction in the americium concentration by a factor of seven was achieved using 3-10g of particles per liter of solution. This is equivalent to a K_d value in the 600-4000 range. Similar tests with plutonium gave concentration reductions of a factor of 50-120 (K_d value in the 3500-6000 range). Stripping tests using alcohol and a variety of stripping agents show a reduction in K_d values to less than 10.

Micrographs of uncoated, commercially available magnetic particles have allowed a correlation to be established between K_d values and how the particle was made. Magnetization studies on coated, non-coated, and gamma-irradiated particles (to examine irradiation effects on the magnetic separation stage of the MACS process), and cobalt-60 gamma source irradiation studies on the TRU-extracting and Cs-extracting particles have started.

Bradtec has started activities on the testing of Cs removal from simulated tank supernatants and has already eliminated one of the five candidate materials.

COLLABORATION/TECHNOLOGY TRANSFER

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2.4 ADVANCED CHEMICAL SEPARATIONS FOR THE CLEAN OPTION

TASK DESCRIPTION

The purpose of this work is to develop new advanced solvent extraction and recovery processes in support of the "Clean Option" strategy that can reduce the complexity and cost of the chemical pretreatment of dissolved sludge to produce raffinates and effluent streams that will meet specifications of Class A low-level waste. The three objectives are to minimize the number of processes needed to achieve "Clean" status, to minimize the number of times that the initial volume of dissolved sludge must be handled, and to concentrate the product streams so as to reduce the scale of the operation to the smallest possible level. The requirements for an advanced chemical separations system that must meet this goal are that it must readily achieve the required decontamination factors, that it must have sufficient chemical and radiolytic stability, that it should not use highly hazardous substances, that it should not significantly increase waste volume, and that an engineering scale-up of the process must be feasible. The new separation scheme comprises a series of novel processes designed to extract and recover thorium, uranium, TRUs (neptunium, plutonium, americium, curium), Sr-90, and Tc-99 from dissolved sludge waste in the Hanford storage tanks (see Figure 2.4).

For example, a combined Strontium Extraction Process/Transuranic Element Extraction Process (SREX-TRUEX) is being examined to extract strontium, technetium, uranium and TRUs and to partition uranium and technetium from strontium and TRUs; a combined SREX-PUREX is being examined to separate strontium, neptunium and plutonium from americium, lanthanides and barium; a new technetium extraction process is being examined to separate technetium from uranium; an actinide/lanthanide resin is being examined to separate americium from lanthanide; and Diphonix™ ion exchange resin is being examined to separate barium and lanthanides from thiocyanate solution.

TECHNOLOGY NEEDS

The advanced chemical separation processes (TOREX flowsheet) will be applicable in the chemical pretreatment of waste retrieved from storage tanks at DOE defense establishments (e.g. Hanford, Savannah River, etc.). The objective of these processes is to minimize the amount of waste that must be vitrified by reducing the level of alpha activity and reducing the concentrations of Sr-90, Cs-137, and Tc-99 in the dissolved sludge waste.

ACCOMPLISHMENTS

A process solvent has been successfully developed that is capable of removing in a single process thorium, uranium, neptunium, plutonium, americium, the lanthanides, strontium and technetium from synthetic dissolved sludge waste from the Hanford single- and double-shelled storage tanks. The TRU elements (neptunium, plutonium and americium) and strontium are then selectively stripped from the uranium and technetium. The latter point is of interest since one does not then need to vitrify uranium. A technetium specific resin has been developed to remove technetium from uranium, thus the uranium fraction is suitable for recycle.

The concentrated TRU-strontium product stream is then treated by the SREX-NEPEX (strontium extraction-neptunium/plutonium extraction) process. A process solvent, similar to the front end process solvent that separates strontium, neptunium and plutonium from barium, the lanthanides and americium, has been developed. A major feature of this process is that barium can now be separated from strontium; this is necessary to minimize the number of glass canisters needed to hold the waste in the geologic repository. The raffinate (barium, the lanthanides and americium fraction) is now a suitable feed for the americium/lanthanide separation system.

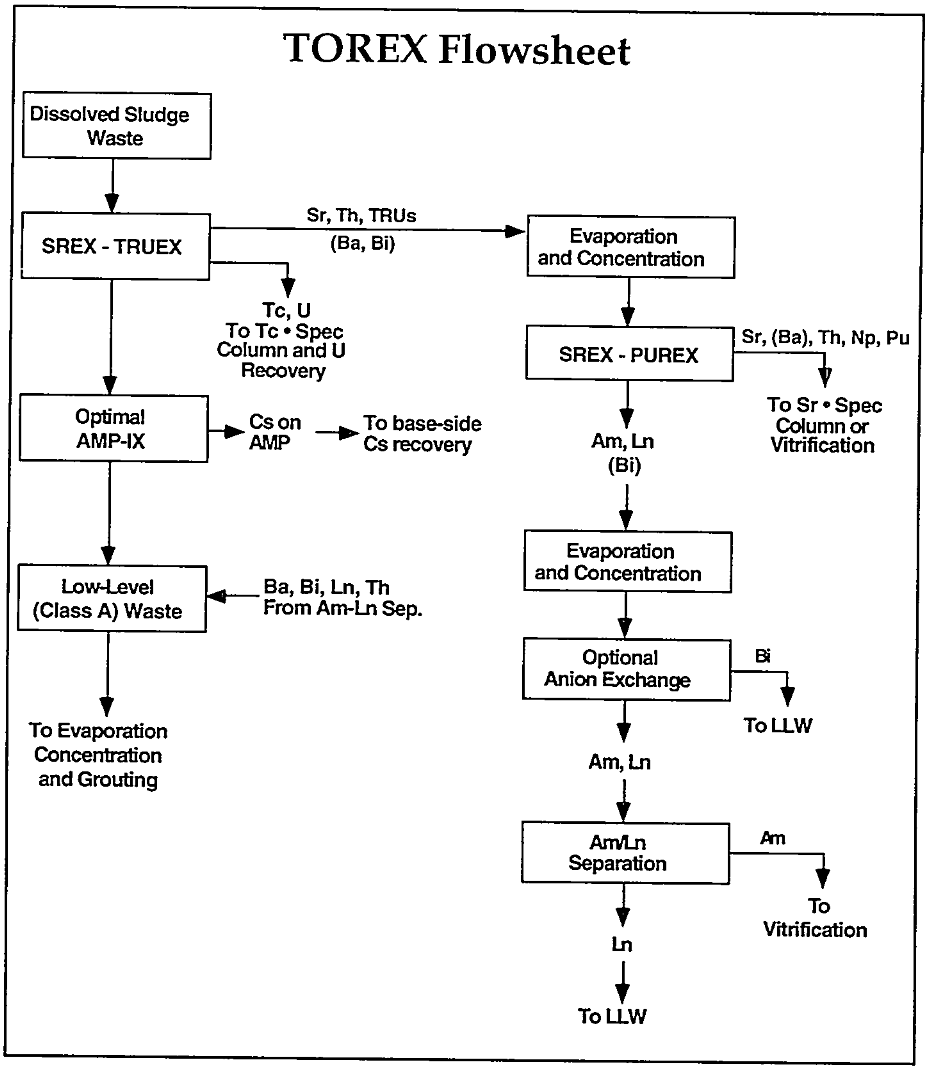

Figure 2.4. A Total Radionuclide Extraction Process Flowsheet.

COLLABORATION/TECHNOLOGY TRANSFER

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2.5 AQUEOUS BIPHASIC SYSTEMS FOR RADIOACTIVE WASTE PRETREATMENT

TASK DESCRIPTION

This project seeks to develop aqueous biphasic separation (ABS) systems for the pretreatment of supernatant solutions from underground storage tanks. The ABS permit the extraction and recovery of dissolved inorganic ions from high ionic strength, acid or alkaline electrolyte solutions. The ABS systems can be generated by the addition of polyethylene glycols to high ionic strength electrolyte solutions. The primary objective is to remove long-lived radionuclides such as Tc-99, I-129, and Se-79 from alkaline solutions. The selective removal of these species by aqueous biphasic separation could be coupled with ion-exchange processes to remove cationic species, such as Cs-137 and TRUs, from alkaline solution. This would permit near-surface disposal of the bulk of the alkaline supernatants and dissolved salt cake from underground storage tanks. The extractions could be carried out without pH adjustment and the only reagent added to the waste stream would be a minimum amount of water to ensure dissolution of the salt cake.

TECHNOLOGY NEEDS

Near-surface disposal of single-shell tank supernatants, after conversion to grout, would require that long-lived isotopes such as I-129, Tc-99, and Se-79 be removed. Ion exchange technology for removal of Cs from alkaline solutions is well developed, while little or no technology is available for recovery of iodine, technetium, or selenium from high-ionic strength alkaline solutions. Acidifying the supernatants would be required for recovery of Tc and Cs by TRUEX or SREX processes and would thereby result in significant increases in waste volume. The process effluents would then have to be made alkaline again before conversion to grout. In addition, Tc, I, and Se are not well extracted by TRUEX, and recovery of Cs requires the use of a crown ether extractant in the SREX solvent.

ACCOMPLISHMENTS

Several tank waste supernatants have been prepared. Aqueous biphasic formation has been demonstrated with SY-101, NCAW, and SST wastes at 25° and 50°C. Aqueous biphase formation has been obtained with polyethylene glycols (PEGs) having average weights of 1500, 2000, and 3400. Partition coefficients for TcO_4^- have been measured giving values that range from 12 to 50 depending on the choice of waste simulant. Irradiation of the PEG phase up to 20 Mrad had no detectable effect on partition coefficients. This dose approximates the yearly dose that would be received by the solvent in processing tank waste from SY-101. We have also irradiated PEG-1500 and PEG-3400 to 75 Mrad. At this higher dose, PEG-3400 began to show evidence of gel formation due to polymer crosslinking, but the lower molecular weight PEG showed no noticeable change in solution viscosity. The lower molecular weight PEGs thus appear to be highly resistant to damage by radiolysis (see Figure 2.5).

The partition coefficients of inorganic species present in the waste simulants have been measured at 25° and 50°C. The partition coefficients for these species are all less than one.

Increasing temperature has the effect of depressing the partition coefficients. However, the opposite effect was observed with technetium in which partition coefficients increased with increasing temperature.

COLLABORATION/TECHNOLOGY TRANSFER

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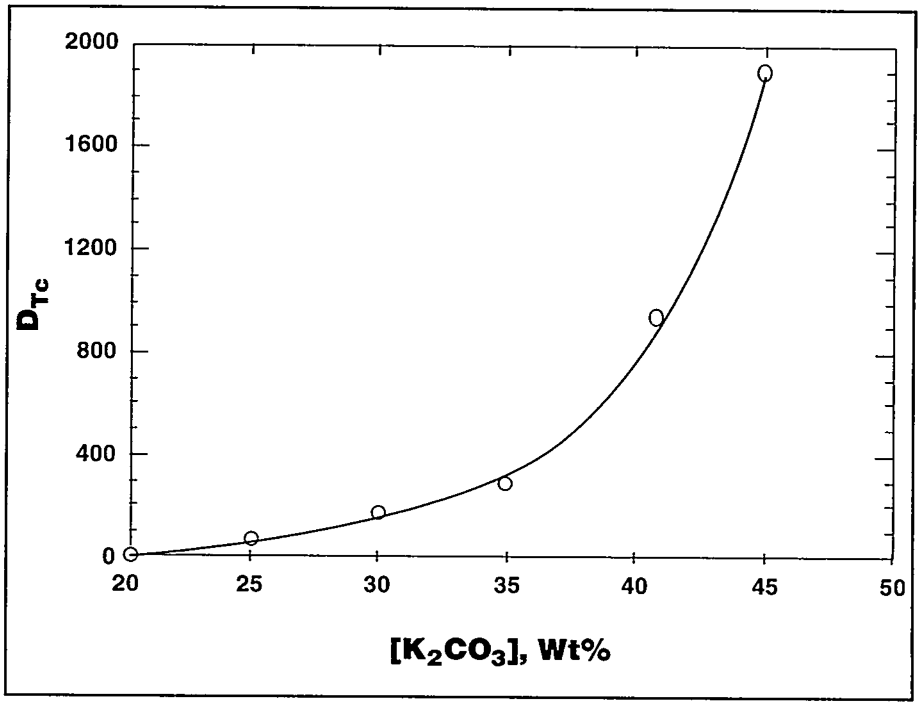

Figure 2.5 Extraction of TcO_4^- From K_2CO_3 By PEG-200.

2.6 BIOCATALYTIC DESTRUCTION OF NITRATE AND NITRITE

TASK DESCRIPTION

The purpose of this task is to develop an enzyme-based reactor system for the reduction of nitrate and nitrite to N_2 and H_2O. It will demonstrate the validity of using immobilized enzymes coupled with biphase partitioning to efficiently destroy nitrate and nitrite. The reducing equivalents are provided by a low-voltage electrical current, which transfers electrons from the cathode to the enzymes via an electron transfer dye. The biphase system is necessary to protect the enzymes from excessive concentrations of electrolytes, especially H+ and OH- which would result in enzyme inactivation, while simultaneously allowing the transfer of nitrate and nitrite from the waste stream to the catalytic chamber. The use of enzymes enables very large specific catalytic activity to be obtained without the need for additional chemical reagents or the production of secondary waste streams (see Figure 2.6).

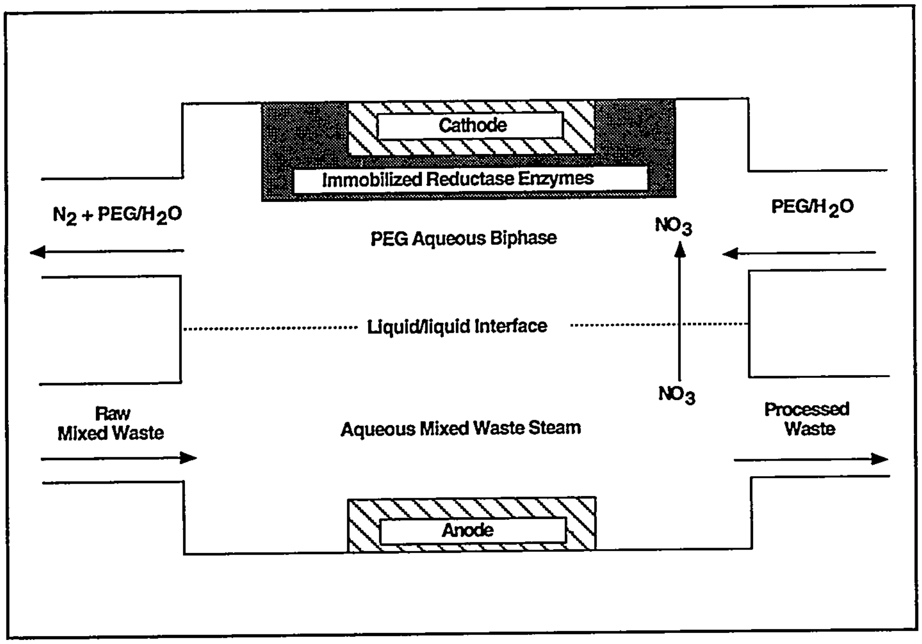

Figure 2.6. Process Description.

TECHNOLOGY NEEDS

The final product of this development effort would be a compact reactor system that could be used to treat aqueous mixed waste and low-level radioactive waste. The high nitrate and nitrite content of these liquid wastes significantly increases the volume of grout produced due to its low capacity for these materials. Nitrate also produces significant quantities of secondary waste.

ACCOMPLISHMENTS

This is a new project in FY94. If the first year's efforts to convert nitrate to nitrite are successful, the efforts in FY95 will focus on immobilization of the remaining enzyme systems necessary to reduce nitrate directly to N_2 and H_2O.

COLLABORATION/TECHNOLOGY TRANSFER

The reactor test using simulated feeds will be carried out jointly between ANL and the University of Iowa. Work at ANL will focus on development of a biphasic extraction system and process integration. Researchers at the University of Iowa will provide support in developing enzyme immobilization techniques and assays of activities.

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2.7 FIXED HEARTH PLASMA ARC TREATMENT PROCESS

TASK DESCRIPTION

A fixed hearth plasma arc thermal treatment unit utilizes a DC-arc generated in a gas flowing between two electrodes. For solid materials, one electrode is the torch, while the other is the material being treated. Energy is resistively dissipated in the arc in the form of heat and light as the electric current flows through the gas between the electrodes. Joule (resistance) heating generates plasma temperatures in the gas (on the order of thousands of degrees Centigrade), which directly heats the wastes in the fixed hearth thermal treatment unit. Organics are destroyed, while metals and inorganics are melted. A vitrified (glassy) waste form is the final product of the process.

Plasma arc thermal treatment technology is characterized by high-efficiency destruction of organics, encapsulation of heavy metals and radionuclides in the vitrified final waste matrix, maximum reduction of waste volume, low off-gas rates, and the capability of processing many waste types in a single-step process.

Under plasma arc technology development and application projects, representative surrogate waste streams will be treated in a plasma arc furnace to determine the applicability of the technology and any unique processing requirements. Surrogates will initially not contain radioactive components. Partitioning of radionuclide surrogates will be determined, and a design for a second generation plasma arc furnace which will safely treat mixed low level (radioactive) wastes will be developed and tested. Waste stream characteristics which are required for processing will be determined, and the project staff will work with regulatory entities to determine the minimal character-

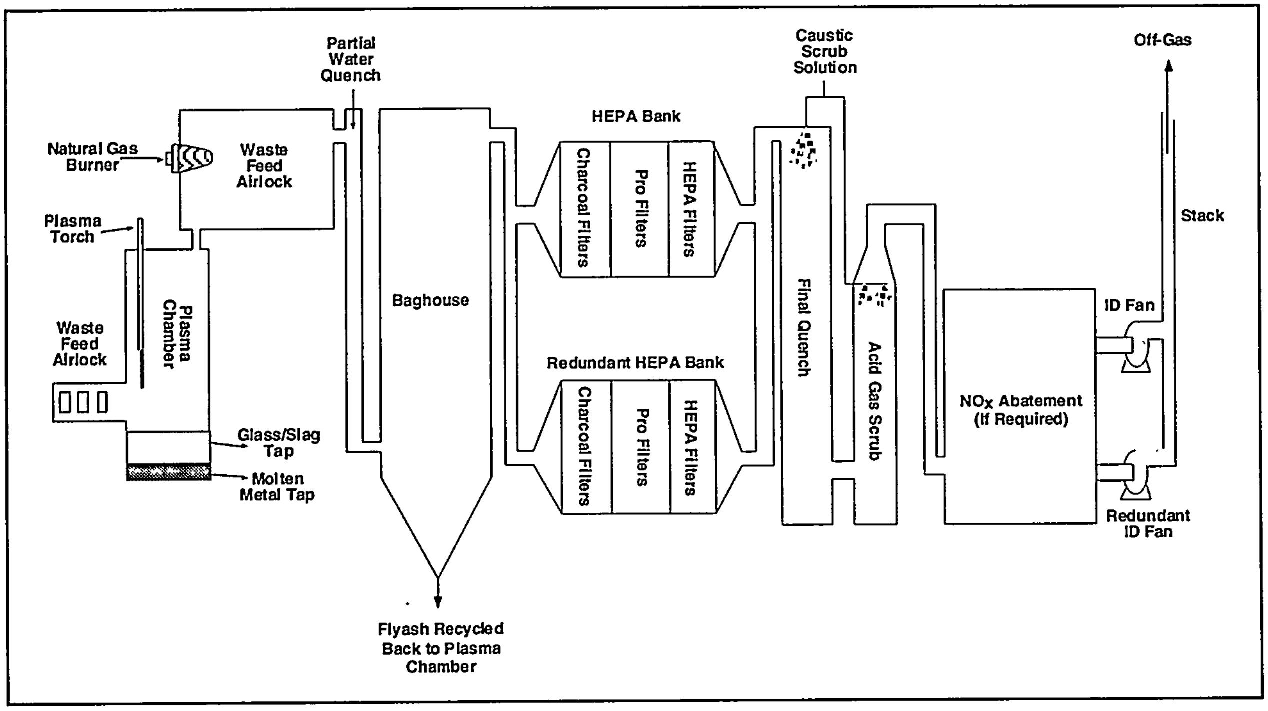

Figure 2.7. PHP Prototype Design.

ization parameters required to meet regulatory requirements while ensuring process safety and effectiveness. Representative final (vitrified) waste forms produced by the process will be evaluated for their performance with respect to leachability, mechanical strength, integrity, and other parameters which will be determined under the project (see Figure 2.7).

TECHNOLOGY NEEDS

Waste streams under the responsibility of DOE are heterogeneous and, as a result of the conditions under which the waste streams were historically generated, are poorly characterized. Detailed characterization of these wastes would incur significant costs. Technologies are needed, therefore, that can treat wastes, meet permit requirements, and satisfy process monitoring needs, with minimal waste stream (feedstock) characterization and segregation requirements. Further, treatment technologies are needed that dramatically reduce waste volumes and that produce final waste forms that are disposable, that is, that will be accepted by a final waste disposal site.

The fixed hearth plasma arc process provides a relatively near-term solution to these technology needs. Plasma arc technology has been in industrial use for many years for metal ore smelting, metal and refractory production and recycling, and metal cutting and welding. Plasma arc thermal treatment units are commercially available for treating non-radioactive industrial and municipal wastes. The Fixed Hearth Plasma Arc mixed low-level waste treatment development project represents a relatively low-risk modification and application of a proven technology to DOE's unique low-level radiological and hazardous waste stream processing requirements.

ACCOMPLISHMENTS

Proof-of-concept test burns have been performed for materials in drums characteristic of DOE's waste streams but without the radioactive components. Wastes were effectively destroyed in the process and produced a vitrified, high-integrity final waste form.

COLLABORATION/TECHNOLOGY TRANSFER

The plasma arc process can accept a wide variety of waste types including paper, cloth, plastics, metals, glass, soil, and sludges. The ongoing projects are directed to demonstrate the application of the plasma arc process to representative surrogate waste streams. This project is a collaboration between Idaho National Engineering Laboratory (INEL), ORNL, MSE, Science Applications International Corporation and RETECH. The Principal Investigators on these plasma arc projects will work with the Mixed Waste Integrated Program (MWIP) Program Manager (HQ/USDOE) to ensure that a high level of awareness of the capabilities of this technology is maintained in the waste treatment community, both within and external to DOE.

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2.8 WASTE FORM PERFORMANCE CRITERIA

TASK DESCRIPTION

Uniform final waste form performance criteria and testing and evaluation methods will allow comparison of alternate technologies for treatment systems and comparisons of waste forms, to ensure long-term waste form safety and stability in storage and disposal and demonstrate compliance with existing orders and regulations. Standardized test methods will improve QA/QC, and testing would generate performance data that could also be used as input to models for site performance assessment (PA) as required by DOE Orders.

TECHNOLOGY NEEDS

Testing procedures have been established by several government and nongovernment organizations: NRC, EPA, IAEA, ASTM. These need to be evaluated for their applicability to mixed waste. Uniform waste form performance criteria will be used to demonstrate that newly developed technologies meet applicable standards, and to support delisting petitions.

Historically, DOE has considered waste form characteristics to be of secondary importance, compared to the hydrogeochemical characteristics of the disposal site. Experience gained in operating LLW disposal sites has shown that waste forms play an important role in the isolation of radioactivity and toxic components of the waste. The lack of uniform waste form performance criteria within the DOE Complex has resulted in large volumes of solidified waste that have failed, due to chemical incompatibility between the waste and solidification materials or poor mechanical properties. These wastes are unacceptable for disposal and are presently being stored at the sites for eventual reprocessing at additional cost.

ACCOMPLISHMENTS

A preliminary draft on final waste form performance criteria has been written and is currently undergoing peer review for comments. The performance criteria specifically examine glass compressive strength and resistance to the release of radionuclides under wet conditions.

COLLABORATION/TECHNOLOGY TRANSFER

This work is being performed in collaboration between BNL, INEL, and Battelle PNL, with BNL as the lead.

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2.9 CHEMICALLY-BONDED CERAMICS FOR STABILIZING PROBLEM LOW-LEVEL MIXED WASTE STREAMS

TASK DESCRIPTION

ANL will fabricate ceramic phosphates as an alternative final waste form. Waste streams that cannot be treated with vitrification will be examined, which include liquid mercury, mercury contaminated liquids, toxic metal materials, salt cakes, pyrophorics and beryllium. Guidelines and assessments will be set up based on the waste stream with the best treatability performance, and that stream will then be scaled up for pilot study (see Figure 2.9).

Metallic oxide contaminants, such as BeO and HgO, and phosphoric acid may be processed into hydrophosphates by reaction at room temperature. This low-temperature processing occurs quickly, minimizing worker exposure and costs. Ceramic phosphates are also nonflammable, insoluble in ground water and stable at higher temperatures.

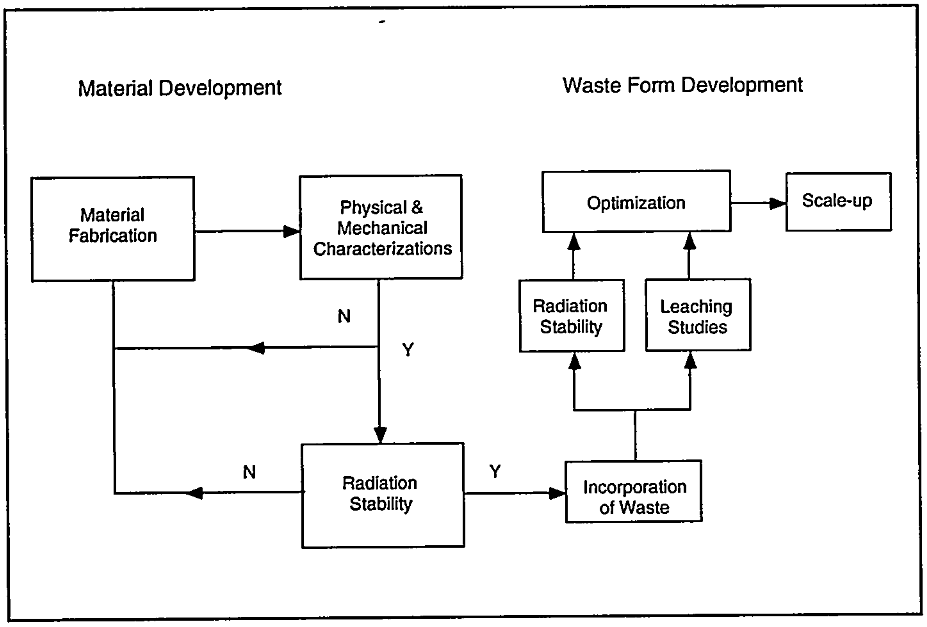

Figure 2.9. Material Development and Waste Form Development.

Plans for FY94 include:

- fabrication of phosphate systems;
- incorporation of surrogate and actual waste into the host phosphates;
- selection of waste streams for a pilot scale study;
- identification of scale up factors and implementation of the pilot scale study; and
- evaluation of pilot scale study leading to improvements of the final waste form.

TECHNOLOGY NEEDS

Alternative methods to mixed waste remediation must be examined for waste streams that cannot be stabilized through vitrification. Incineration and vitrification at higher temperatures produce secondary waste which must be further treated by the off-gas process which increase costs. Chemically bonded ceramic phosphates can decrease costs incurred from secondary waste due to solidification and stabilization at lower temperatures.

ACCOMPLISHMENTS

Aluminum phosphate and magnesium ammonium phosphate ceramics have been synthesized at room temperature. Initial leaching studies show they are suitable for containment of mixed waste.

COLLABORATION/TECHNOLOGY TRANSFER

The University of Illinois at Urbana-Champaign will have input with the phosphate project through professor and graduate student involvement and lab time. BNL intends to treat similar waste streams with polymeric binders. Future contacts and collaborations between ANL and BNL have been established to discuss the differences between these two approaches. Industry partners will be established when the project begins its pilot scale up.

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2.10 MIXED WASTE TREATABILITY USING ALTERNATIVE POLYMER FINAL WASTE FORMS

TASK DESCRIPTION

BNL has identified non-thermal stabilization mechanisms for waste streams that cannot be stabilized by vitrification. Polyethylene encapsulation and modified sulfur concrete encapsulation are thermoplastic methods that can stabilize mercury and chloride salts. Polymer impregnated concrete can stabilize tritiated aqueous wastes.

Plans for FY94 include:

- submittal of Project Test Plans for the three alternative systems;
- surrogate waste production;
- incorporation of surrogate wastes into polyethylene encapsulation and modified sulfur concrete encapsulation systems;
- incorporation of tritiated aqueous wastes into the polymer impregnated concrete system;
- final waste form evaluation for the processes; and
- full-scale demonstration of the thermoplastic encapsulated technology showing the most promising treatability results. These technologies will be applied to other waste streams that cannot be treated by incineration or vitrification.

TECHNOLOGY NEEDS

Liquid mercury, chloride salts and tritiated aqueous waste streams are not easily treated by incineration or vitrification methods. DOE facilities at Oak Ridge, Savannah River, Fernald, Hanford and Rocky Flats need improved technologies for these areas.

ACCOMPLISHMENTS

Previous polymer encapsulation work at BNL for chloride and fly ash contaminants has established equipment and resources. Results have been obtained showing extremely low leachability. The process flow charts for the polyethylene encapsulation, the modified sulfur cement encapsulation and the polymer impregnated concrete are shown in Figures 2.10a, 2.10b, and 2.10c.

COLLABORATION/TECHNOLOGY TRANSFER

BNL has received approval for a CRADA with Specific Nuclear, commercial radwaste services in Columbia, South Carolina, to fund the polyethylene encapsulation process. Industrial partnership for the modified sulfur cement encapsulation will be identified upon pilot scale- up work.

BNL will continue to coordinate alternate final waste form characterization with other MWIP projects, such as the ceramic phosphate work at ANL. Future collaborations will involve Ames Lab for process monitoring

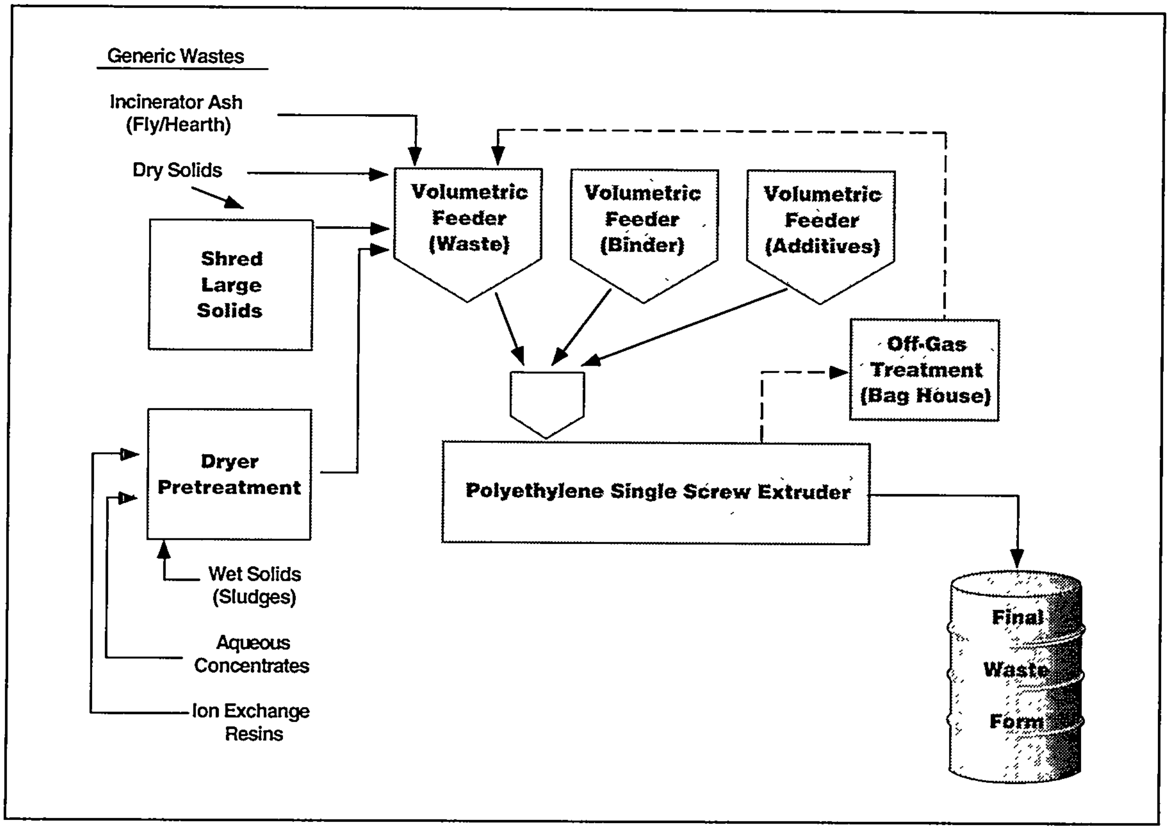

Figure 2.10a. Polyethylene Encapsulation Process Flow.

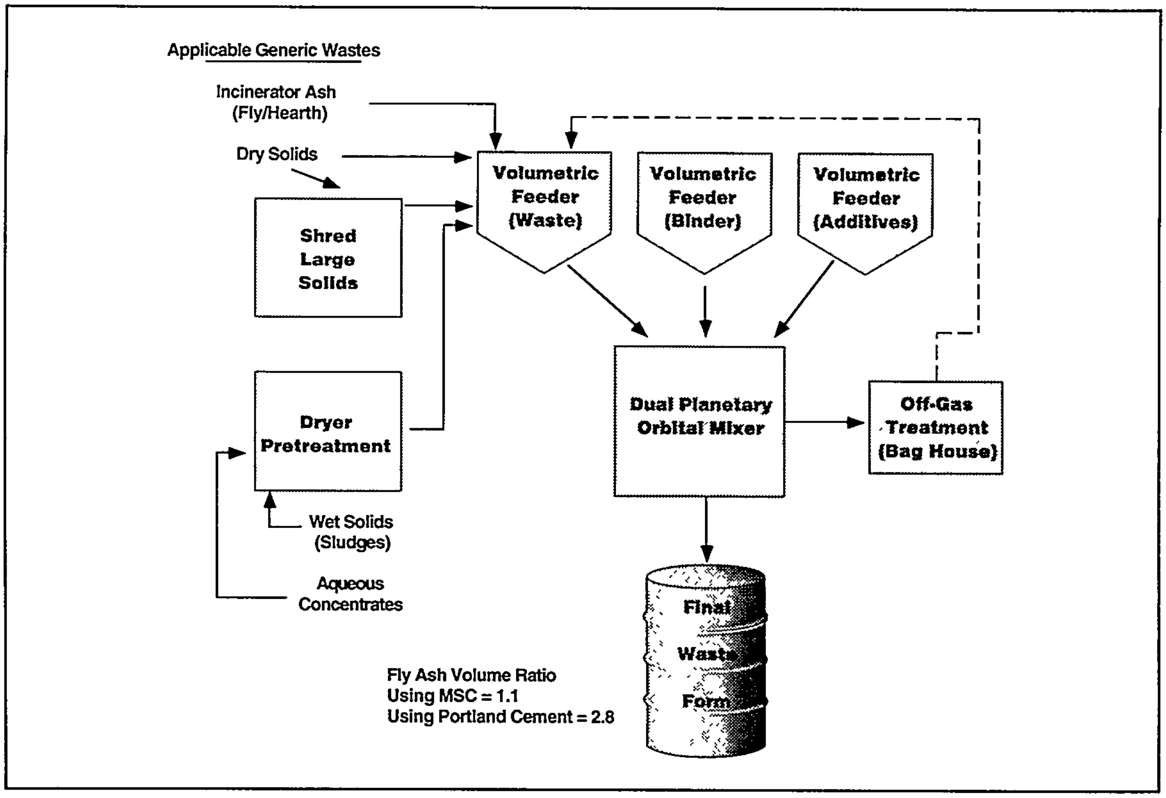

Figure 2.10b. Modified Sulfur Cement Encapsulation Process Flow Diagram.

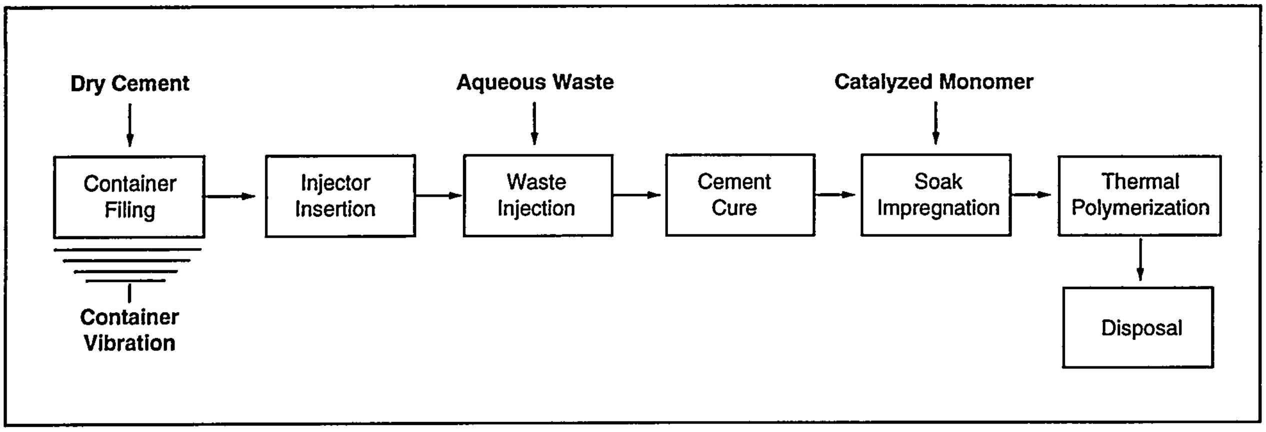

Figure 2.10c. Conceptual fixation of aqueous waste in polymer impregnated concrete by the injection technique.

systems and the University of Cincinnati for non-destructive evaluation of the final waste form.

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2.11 TREATMENT CONTROL STRATEGIES AND TECHNOLOGIES FOR IMPROVED PROCESS CONTROL, SAFETY AND EFFICIENCY

TASK DESCRIPTION

The principal characteristic that differentiates DOE's environmental remediation and waste management requirements from those associated with regulated hazardous and toxic waste is the radiological component of DOE's waste streams. Radioactive transuranic elements and elements of the actinide series must be controlled under DOE regulations. The public expectation is that radiological components will be strictly controlled and continuously monitored while under processing to avoid the unintended (uncontrolled) release of radionuclides to the atmosphere or other phase compartments in which radionuclides could be mobile (e.g., soil, groundwater) and pose a threat to human health or the environment.

MWIP is seeking to ensure that technologies are available to monitor, on a real-time and continuous basis, radionuclides, hazardous metals and other components of mixed wastes that must be treated for disposal and/or delisting under such environmental regulations as RCRA. MWIP intends to accomplish this goal by identifying and characterizing the state-of-the-art of process monitoring sensors and instruments, process control and optimization algorithms, and gaps in required technologies, and, by sponsoring or co-sponsoring technology development programs, to fill identified technology gaps in DOE's unique Mixed Low-Level Waste (MLLW) treatment programs.

TECHNOLOGY NEEDS

Process characterization, monitoring and control technologies are needed to ensure that uncontrolled releases of radionuclides to the environment do not occur in DOE's hazardous and toxic waste treatment processes. Additionally, improved process characterization, monitoring, and control technologies for MLLW are necessary to ensure worker health and safety, to reduce costs of processing MLLW, and to ensure that waste volumes are reduced through optimization of integrated treatment processes.

ACCOMPLISHMENTS

MWIP is currently supporting the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University. DIAL is developing Fourier Transform Infrared Spectrometers, Coherent Anti-Stokes Raman (CARS) Spectrometers, and Laser Optogalvanic Spectrometers (LOGS). These methods can detect atomic and molecular species (including metals) in waste streams and on surfaces. A laser Doppler velocimeter has been demonstrated to measure flow velocities to 1,500 meters per second. Various remote temperature measurement systems are under development or testing, including an optical pyrometer, LOGS, a potassium emission/absorption system (PE/AS), and CARS. An extractive gas analysis system has been developed and tested for carbon monoxide, carbon dioxide, sulfur dioxide, molecular oxygen, nitrous oxides (NOx), and hydrocarbons. A self-cleaning optical port has been developed that can blow off any slag formed over its entry port in combustion chambers or off-gas systems.

MWIP has sponsored the development of surrogate waste to develop and test instrumentation and treatment methodologies in facilities that are not permitted for treatment of specific radiological/hazardous (mixed) wastes. MWIP intends to perform live tests of its technologies under development in a permitted facility to ensure that its technologies are providing the capabilities intended and to assist in design and permitting efforts. An additional critical goal of developing and executing live tests is to develop concrete specifications to guide the development of monitoring and control technologies.

MWIP is investigating process monitoring and control technologies for application to DOE treatment processes. This investigation encompasses traditional monitoring and control strategies and is being extended to encompass artificial intelligence expert systems, fuzzy logic, and neural network systems. Integration of these technologies should provide a reliable sensor fusion/process monitoring and control capability which can detect excursions from desired process conditions and rapidly correct process set points to contain any such excursions. This predictive capacity, will provide DOE with the capability to simulate processes and excursions from desired behaviors to investigate means to avoid such excursions before waste processing begins. Additionally, the predictive capacity to be developed will permit the rapid integration and optimization of treatment processes.

COLLABORATION/TECHNOLOGY TRANSFER

MWIP has co-sponsored a workshop to identify characterization, monitoring, and process control requirements and available technologies. MWIP is developing relationships with industry to ensure that available capacities are not overlooked and to encourage industry's participation in technology development and transfer. MWIP is currently developing a TASR that will catalog available technologies, technologies under development, points of contact within DOE, general requirements, and vendors of technologies. MWIP is implementing a policy that requires private sector (industrial and academic) participation in its technology development activities.

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Pollution Prevention

Section 3.0

3.0 POLLUTION PREVENTION PROGRAM OVERVIEW

Manufacturing processes generate much of the hazardous waste within DOE, other Federal agencies, and U.S. industry. EPA estimates that the national cost of pollution control, treatment and disposal in 1990 was almost $115 billion, with industry's share at about $73 billion.[3] The Office of Technology Assessment estimates that 99 percent of these costs are for end-of-pipe pollution control.[4] Recognizing that pollution prevention is the preferred alternative, DOE has established a national research program for pollution prevention and waste minimization at its production plants. During FY89/90 EM, through OTD, established a comprehensive pollution prevention technical support program to demonstrate new, environmentally-conscious technologies for production processes.

DOE/EM is responsible for the dismantlement of approximately 2,000 weapons per year; requiring the treatment of approximately 230 m^3 of components yearly. DOE estimates that a 10-fold reduction in waste volume is possible through advanced processes and technologies resulting in an annual storage cost savings of about 95 percent, from $2.8 million to $112,000. In addition, EM estimates indicate that innovative resource recovery processes could provide approximately $10 million per year through the resale of precious metals such, as silver, gold, and platinum.

EM, together with other agencies and industry, is developing technological solutions to address common waste stream problems, such as chlorinated solvents, toxic metals from finishing operations, VOCs from cleaning operations, and waste acid recycle. For example, EM works closely with the electronics and electro-manufacture process industry to develop manufacturing processes and associated technologies, that reduce or eliminate the use of chlorinated fluorocarbons and chlorinated hydrocarbons. DOE estimates that it uses in excess of 180,000 liters of chlorinated hydrocarbons in cleaning electronic components annually. EPA estimates indicate that contaminated soil, sediment, and sludges at sites listed on the National Priorities List (those with RODs) from electronic/electrical equipment alone approach 1.5 million cubic yards.[5]

The Pollution Prevention program supports an integrated approach to pollution prevention and waste minimization by developing and demonstrating technologies that focus on process modifications, material substitutions, recycling and reuse, and energy efficiency in support of applicable Federal, State and local environmental regulations. Advances in this area have the potential to provide significant cost savings through efficient use of raw materials and lower costs associated with waste storage, treatment, and disposal. In addition, they may stimulate U.S. competitiveness and economic growth through the growth of a "clean" technology industry.

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[3] U.S. Environmental Protection Agency, Office of Policy, Planning and Evaluation, Environment Investment: The Cost of a Clean Environment, EPA-230-11-90-083, November 1990.

[4] U.S. Congress, Office of Technology Assessment, Serious Reduction of Hazardous Waste: For Pollution Prevention and Industrial Efficiency, OTS-ITE-317, September 1986.

[5] U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response Technology Innovation, Cleaning Up the Nation's Waste Sites: Markets and Technology Trends, EPA-542-R-92-012, April 1993.

3.1 LEAD FREE SOLDER PASTE

TASK DESCRIPTION

This activity recommends development of lead-free solder alloy pastes which may be used in environmentally acceptable circuit assembly by means of surface mound technology. The subtasks involve alloy design and selection, preparation of ultrafine solder alloy powders, conversion of powders to paste, evaluation of alloy wetting characteristics, solder assembly and performance evaluation of test vehicles, and demonstration of the feasibility of Environmentally Conscious Manufacturing (ECM) on development hardware and transfer of this technology to U.S. industry and war reserve production. In addition to being environmentally safe, the ultrafine powders produced during this project will enable manufacture of printed wiring boards having considerably finer pitch to meet the challenge of today's shrinking microcircuit technologies. Successful completion of this project will ease public anxiety over lead use in manufacturing, and assist U.S. industry in being more competitive in world markets.

TECHNOLOGY NEEDS

Lead metal and its compounds are known toxins, and legislation in both Houses of Congress is staged to ban or heavily tax lead use in all commercial products. Since lead is a component of electronic solder alloys, U.S. electronic manufacturers are concerned that this legislation will unnecessarily burden the industry, which is already reeling from intense overseas competition. This program is developing lead free solder alloy pastes, which may be used in environmentally- acceptable circuit assemblies.

ACCOMPLISHMENTS

- Identified initial lead-free solder candidates by characterization of melting behavior and microstructure of small ingot samples.
- Characterized solder alloy performance in wetting, mechanical strength, ductility, and thermal fatigue.
- Optimized high-pressure gas atomization process for production of fine lead-free solder alloy powder.

COLLABORATION/TECHNOLOGY TRANSFER

The technologies will be available to DOE design and production facilities, subcontractors, other government agencies, and the commercial sector. Technology transfer will be handled through Sandia National Laboratory's (SNL) Technology Transfer Center. Site visits, technical presentations, and documentation in open literature will also facilitate technology transfer.

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Innovation Investment Area

Section 4.0

4.0 INNOVATION INVESTMENT AREA OVERVIEW

The mission of OTD's Innovation Investment Area is to identify and provide development support for two types of technologies: (1) technologies that show promise to address specific EM needs, but require proof-of-principle experimentation, and (2) already proven technologies in other fields that require critical path experimentation to demonstrate feasibility for adaptation to specific EM needs.

The underlying strategy is to ensure that private industry, other Federal agencies, universities, and DOE National Laboratories are major participants in developing and deploying new and emerging technologies. This is accomplished through substantial funding set aside for building public and private-sector partnerships. Tools employed to achieve this include: Program Research and Development Announcements (PRDAs), Research Opportunity Announcements (ROAs), CRADAs, Financial Assistance Awards (Grants), Interagency Agreements (IAGs), and DOE National Laboratory TTPs. Activities procured through these contracting devices can be promptly moved to other RDDT&E programs that identified the need for research and development, or to the private sector for commercialization.

4.1 ELECTROSPRAY MASS SPECTROMETRY FOR RAPID MEASUREMENT OF RADIONUCLIDES, TRACE ELEMENTS, AND ELEMENTAL SPECIATION

TASK DESCRIPTION

The purpose of this project is to develop a single instrument for radionuclide measurement, trace element analysis, and characterization of elemental speciation.

Experimentally, the project will focus on the direct discrimination of elemental isobars such as ^{238}PU and ^{228}U, using a capillary electrophoresis (CE) and electrospray mass spectrometry (EMS). Both CE and EMS are highly-developed analytical techniques with widespread applications.

In CE, the elements of interest are first separated using an aqueous environment. In EMS, electrically charged droplets are created from the liquid sample obtained by CE. As the solvent evaporates, free solute ions remain in the gas phase. The solute ions are then extracted into a vacuum system housing a quadrupole mass spectrometry. During the extraction process, the ions are often drawn through a curtain of collision gas to remove solvent further or to induce collision dissociation.

The CE-EMS device to be developed will be smaller and less expensive than other types of mass spectrometers that might be able to distinguish isobars, such as the Fourier transform or resonance ionization mass spectrometers. In terms of absolute detection limits and suitability for real-time analysis of radionuclides, CE-EMS is expected to prove superior to inductively coupled plasma. Additionally, EMS requires much less gas than the ICP and should therefore be easier to incorporate in field-deployable instruments.

TECHNOLOGY NEEDS

Characterization of waste sites, and the associated measurement of contaminants, is an integral part of the clean-up process and is a required element in all stages of remediation. The development of more efficient characterization, monitoring, and sensing technologies will speed up the clean up process and assure more effective remediation. Conventional sampling and analysis approaches rely on expensive and time consuming laboratory analysis of environmental samples. Real-time field analytical methods and technologies are needed to expedite this process and provide decision quality results, so as to ascertain the efficiency of site remediation efforts. In addition, more rapid and specific chemical characterization of a site will permit remediation activities to occur at a faster pace and to be aimed only at contaminated locations.

ACCOMPLISHMENTS

This is a new project. A purchase order was placed with Perkin-Elmer to obtain the necessary analytical equipment. No other significant accomplishments to date have been achieved.

COLLABORATION/TECHNOLOGY TRANSFER

This project was contracted to Ames Laboratory to develop a compact, rugged electrospray mass spectrometer instrument that requires less expandable supplies and is well suited to field use in a van or trailer. Perkin-Elmer has agreed to offer technical support and limited special hardware for interfacing CE with EMS, as well as a discount on the purchase of equipment.

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4.2 A PROCESS FOR CONTAMINANT REMOVAL AND WASTE VOLUME REDUCTION TO REMEDIATE GROUNDWATER CONTAINING CERTAIN RADIONUCLIDES, TOXIC METALS, AND ORGANICS

TASK DESCRIPTION

The aim of this project is to develop and demonstrate an improved ex situ treatment process for removing groundwater contaminants.

A combination of process steps will be used consisting of sequential chemical conditioning, microfiltration and dewatering by low-temperature evaporation and/or filter pressing to achieve high contaminant removal efficiencies.

The experimental program will focus on performing screening tests to identify key process variables. Key variables to be evaluated include: type and composition of waste influent to the process; precipitation conditions; type of ion exchange/adsorbent material, their concentration and treatment condition; type and concentration of non-contaminant metals; type and concentration of leaching agent for soil washing; and conditions to solidify secondary waste produced by the process (see Figure 4.2).

The conditioning of the contaminated water by a sequential addition of chemicals and adsorption/ion exchange materials produces a polydisperse system of size enlarged complexes of the

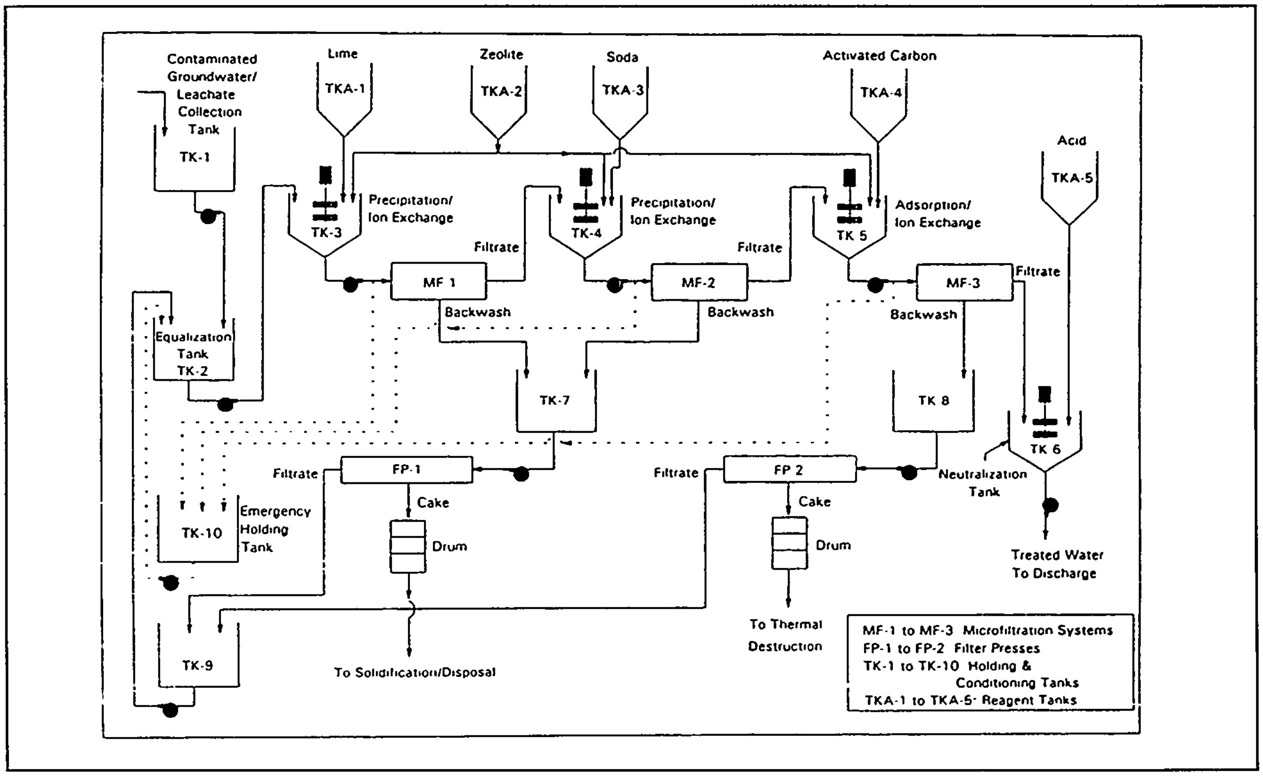

Figure 4.2. A Schematic of the Chemical Treatment-Microfiltration Process.

contaminants in three distinct configurations: water soluble metal complexes, insoluble metal precipitation complexes and contaminant-bearing particles of ion exchange and adsorbent materials. Waste volume is reduced by dewatering of the polydisperse system by cross-flow microfiltration, followed by low-temperature evaporation. The bulk of the filtrate is discharged if it meets the specified target water quality, or is recycled.

TECHNOLOGY NEEDS

Groundwater at many of the DOE sites has been contaminated with radionuclides, heavy metals, and organic compounds. To protect public health and the environment, both ex situ and in situ technologies are needed to treat the contaminated groundwater.

Ex situ purification of aqueous solutions can be achieved by a variety of methods. The process described here integrates a number of standard unit operations including ion exchange, neutralization, precipitation and evaporation. The end product is a process that will generate high quality effluent while minimizing secondary waste volume.

ACCOMPLISHMENTS

- Overall test results revealed a three-step chemical treatment/microfiltration sequence combined with a final dewatering step is optimal for effective treatment of mixed waste having diverse physico-chemical properties.
- Key chemical treatment steps include: pH adjustment by lime addition combined with zeolite heavy metals. Sequential addition of natural zeolite ion exchange/adsorbent powder to remove radionuclides, and sequential addition of powdered activated carbon with or without zeolite powder as a polishing step to remove organics and residual radionuclides.
- The use of $FeCl_3$ as the leachant to extract Strontium-90 from the contaminated soil showed a synergistic effect: excellent strontium-90 removals from the soil at low concentrations at room temperature; and effective in the removal of metal ions in the first step of the laced treatment by coprecipitation and adsorption-scavenging.
- Process economics were assessed for treatment plants of 2 and 300 gpm throughput capacities. Installation costs are estimated at $275,000 for the 2 gpm plant, and at $4 million for the 300 gpm plant, while annual operating costs are estimated at $418,000 and $12 million for the 2 gpm and 300 gpm plants respectively, including secondary waste disposal and capital recovery costs.

COLLABORATION/TECHNOLOGY TRANSFER

A simplified, single-stage version of the process was successfully implemented to treat groundwater and surface water contaminated with Strontium-90 at the Chalk River Laboratories (CRL) site in Chalk River, Ontario, Canada.

This technology will undergo additional trials at CRL that will include more detailed and complete analyses of its capacities to remediate radioactive and chemically hazardous waste solutions and groundwaters.

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4.3 ASSESSMENT OF SUBSURFACE VOCS USING A CHEMICAL MICROSENSOR ARRAY

TASK DESCRIPTION

The objective of this project is to demonstrate applications of coated surface-acoustic-wave (SAW) microsensors for use in site monitoring, assessment and restoration activities at waste sites.

SAW devices function by generating mechanical (acoustic) waves along the surface of a piezoelectric quartz substrate. The devices respond with high sensitivity to changes in surface mass, and, as a result, they can be used for a wide range of potential organic vapor analytes. Sensitivity to and selectivity for VOCs are achieved by coating the SAW device with a polymer or high-boiling liquid into which the vapor will reversibly partition: vapor sorption increases the mass of the surface coating and causes a proportional shift in the oscillation frequency.

The coated-SAW sensor response depends on vapor-coating interactions and the frequency of the oscillator. In general, the sensor response (frequency shift) is linear with concentration. Selectivity for vapors and gases can be achieved by utilizing appropriate coatings. Because vapor-coating interactions have varying degrees of selectivity, pattern recognition approaches are used to interpret sensor array output and improve discrimination.

Sensor systems will be configured to minimize dead volume and to maximize thermal stability. The instrument that will be developed and investigated has an array of four SAW sensors that operate at a frequency of 158 MHz and an internal, four-channel frequency counter. The instrument occupies a volume of about 0.3 ft^3 and consumes about 2W of electrical power.

Work will focus on six compounds that are representative of three classes of organic compounds: halocarbons, aromatic hydrocarbons, and saturated aliphalics. Fourteen coatings capable of rapidly and reversibly absorbing organic vapors will be tested. Thin (<1 μm) coatings will be applied to SAW devices using an air-brush. Coatings will be tested for vapor concentrations ranging from low ppm to near saturation at the experimental conditions of 25° C and 50 percent relative humidity.

TECHNOLOGY NEEDS

At many DOE sites, soil and groundwater have been contaminated with VOCs. In site assessment, chemical analyses are needed to identify and quantify the VOC contamination. This project focuses on the demonstration of arrays of microfabricated surface-acoustic-wave chemical sensors which could be reduced in size to fit within a four inch well casing for rapid assessment of VOC contamination in subsurface media. Such instruments would considerably improve the quality and quantity of analytical data used to guide assessment and restoration efforts at contaminated sites.

ACCOMPLISHMENTS

- Tests of all vapor-coating pairs show that while detection limits were somewhat higher than anticipated, results were very reproducible, linear, and the selectivity reasonably high.

- Detection limits varied significantly depending on the vapor being considered, the coatings employed on the sensor array, and the operating temperature. For many VOCs, the limits of detection are in the range of 20 to 500 µg/L (or about 5 to 125 ppm). Recent improvements in SAW sensor design could reduce the detection limits by an order of magnitude.

- Results of headspace analysis were in excellent agreement with predictions based on simple models, e.g., using Henry's law coefficients for partitioning between water and air.
- Results using a pattern-recognition procedure indicate that vapors were correctly identified an average of 95 percent of the time and that vapors could be distinguished both within and between the three chemical classes.

COLLABORATION/TECHNOLOGY TRANSFER

SAW microsensor arrays can identify and quantify VOCs, such as chloroform, benzene, xylene, isooctane, hexane and trichloroethane, typically found at contaminated DOE sites. Furthermore, sensor responses are linear and additive over a wide concentration range, making them suitable for identifying vapor mixtures.

The results obtained in this project support the use of SAW sensor instrumentation for applications such as headspace analysis, soil gas monitoring, and vacuum extraction process monitoring. It may also be possible to develop a battery-powered version for use in wells and pipes and for screening waste drums or performing compatibility analyses.

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4.4 BIODEGRADATION OF CHLORINATED HYDROCARBONS IN A VAPOR-PHASE REACTOR

TASK DESCRIPTION

The objective of this project is to evaluate the feasibility of using a biological treatment system for the vapor phase destruction of chlorinated aliphatic contaminants stripped from groundwater.

The concept of a vapor phase reactor is based upon the introduction of VOCs as gases diluted in an air stream to the biocatalysts in an aboveground reactor. This type of reactor can be used in conjunction with conventional pump and treat methods, as a secondary treatment for off-gases, as a stand-alone system for destruction of harmful air emissions from point sources, and as part of integrated bioremediation systems that include in-situ methods.

The experimental approach will focus on the construction of two bench-scale gas-lift loop reactors with volumes of 3.5 and 7.0 L, containing two biocatalysts: Pseudomonascepacia and Pseudomonas mendocina (see Figure 4.4). The reactor tank contains the biocatalyst as a cell suspension in a nutrient broth. The contaminated air is fed into the reactor as a stream of small bubbles from the bottom of the riser. The gases circulate through the reactor and come into contact with the biocatalysts, where degradation occurs.

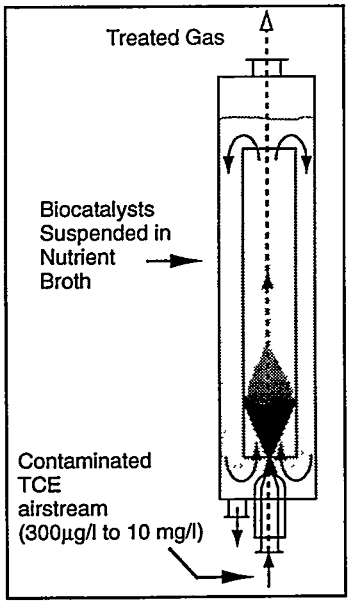

Fig. 4.4: Gaslift Loop Reactor.

Treated gases exit through a port in the top of the reactor. Three other ports are also located at the top of the reactor for the addition of air, the addition of a solution containing the cosubstrate, and the withdrawal of biomass samples. T-fittings will be attached to the inlet and outlet ports of the reactor through which gases will be sampled by gas chromatography with electron capture detection. Automatic sampling and injection systems will be used to minimize human error.

TECHNOLOGY NEEDS

Trichloroethylene (TCE) is believed to be one of the most prevalent organic contaminants of both soils and groundwater at many DOE sites. At present, the most commonly used technologies for TCE removal and/or degradation include vapor extraction, air stripping, catalytic oxidation and adsorption. The first two methods are economical but environmentally unacceptable since volatiles are released directly into the air. Catalytic oxidation and adsorption are costly and operationally complex; the latter is a phase transfer process requiring ultimate disposal or regeneration of the adsorbent. Biological vapor phase destruction might provide a convenient, low cost, reliable alternative for effectively removing VOCs from contaminated groundwater and soils.

ACCOMPLISHMENTS

- A bench-scale vapor-phase reactor for TCE destruction was successfully demonstrated.
- Data shows that TCE degradation by Pseudomonas mendocina can be highly efficient on a cosubstrate usage basis. The degradation of 0.2 to 1 g of TCE requires the consumption of 2 g of phenol with Pseudomonas cepacia or 4 to 8 g of toluene with Pseudomonas mendocina.
- Both micro-organisms could degrade 95 percent of inlet TCE at air flow rates of up to 3 percent of the total reactor volume per minute.
- TCE concentrations between 300 and 3,000 µg/L were degraded with 95 percent or better efficiency.
- The reactor can be operated continuously for at least 14 days and up to 33 days, averaging 95 percent or better efficiency.
- TCE removal efficiencies can be increased to greater than 99 percent by adding a small canister of granulated carbon to scrub the last traces of TCE from the air.
- The biocatalysts are relatively insensitive to system shocks, such as large "spikes" of TCE (in excess of 5-10 mg/L) in the inlet air.
- After exposure to several transient high TCE concentration events over a period of nine days, reactor performance could be restored to removal efficiencies of 90 percent or greater.

COLLABORATION/TECHNOLOGY TRANSFER

The vapor-phase degradation system can be used alone for treating VOCs emitted from point sources. It can also be attached to existing air stripping or vapor extraction systems, replacing more expensive and/or less efficient secondary vapor removal methods such as carbon adsorption or catalytic oxidation for treating off-gases. No ancillary technologies are necessary to utilize this system in these application.

Based in part on the results of this project, Envirogen has constructed a demonstration-scale reactor at its own expense. Envirogen can deploy this system at a mutually agreed-upon DOE site, and test and evaluate the capacity of the bioreactor to destroy TCE from a vapor feed in the field.

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4.5 CHROMATE REDUCTION AND HEAVY METAL FIXATION IN SOIL

TASK DESCRIPTION

The primary objective of this project is to investigate a novel approach for remediating heavy metal contamination in soil.

The approach consists of in-situ reduction of chromates with a ferrous salt, and fixation of the metals using a destabilized aqueous sodium silicate solution. The use of iron, as iron II, fulfills two functions: it reduces available chromate VI to chromate III, the chromate III and iron III thus formed in this reaction are precipitated at soil pH as $Cr(OH)_3$ and $Fe(OH)_3$, and in the precipitation step, other metals are co-precipitated and adsorbed on the hydroxides. In the absence of Cr VI or another oxidized species, Fe III must be substituted for Fe II.

The silica treatment also serves two purposes: it reacts with the metal and metal hydroxides to reduce metal solubility, and it lowers the soil permeability thereby reducing the leaching rate of the treated soils (see Figure 4.5).

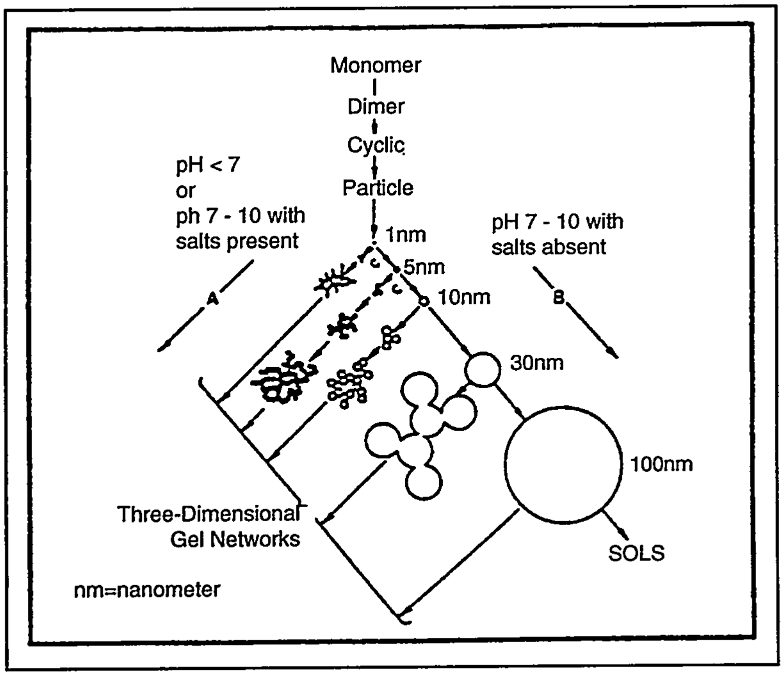

Figure 4.5. Polymerizationbehavior of silica. In basic solution (B) particles in solution grow in size while decreasing in numbers; in acid solution or in presence of flocculating salts (A), particles aggregate into three-dimensional networks and form gels.

TECHNOLOGY NEEDS

Soils at many of the DOE sites have been contaminated with radionuclides and heavy metals. The potential migration of radionuclides and heavy metals from contaminated soils necessitates technologies to treat the contaminated volume in a manner that effectively protects the environment.

In-situ chromate reduction and metal fixation might prevent the migration of contaminants, and provide permanent isolation and containment at an affordable cost.

ACCOMPLISHMENTS

- Test results from three Central Texas soils demonstrated that in-situ Cr VI reduction with Fe II was successful for soils containing up to 400 ppm Cr VI. At higher Cr VI concentrations, treatment in combination with soil washing may be necessary.
- zeolite gel fixation. However, more work in gel refinement is recommended. An extraction pH, using deionized (DI) water, not greater than pH 8.5 - 9.0 is desirable. Above this regime the solubility of silica increases drastically.

- When the leachate flow rate is reduced by three to five orders of magnitude, the leachate concentration is reduced by one to two orders of magnitude.

- Iron plus silica treatment results in a leachate concentration reduction of up to two orders of magnitude (Cr: 95-99%, Pb: 99%; Zn: 95-99%; Cd: 93-99%; Ni: 75-94%).

COLLABORATION/TECHNOLOGY TRANSFER

Experimental results suggest that in-situ silica gel treatment of soils could be used to prevent the migration of contaminants, isolate contaminated volumes, and provide permanent containment of heavy metal contaminants.

The technique should be especially applicable to remediating the fringes around more heavily polluted cores. There, the pollution gradually decreases while the volume of soil to be treated increases exponentially with the distance from the core.

The chemical cost to treat 1 yd^3 is estimated to be around $5.

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4.6 COMBINED AIR STRIPPER/MEMBRANE VAPOR SEPARATION SYSTEMS

TASK DESCRIPTION

The objective of this project is to build and operate a combined air stripper/membrane vapor separation system in which the membrane system removes the VOCs from the air stripper vent stream and recirculates the air to the stripper.

The overall flow diagram of the combined air stripper/membrane vapor separation system is given in Figure 4.6. Air and VOC-contaminated water flow countercurrent through the air stripper, producing a VOC-laden air stream and a VOC-depleted water stream.

The VOC-laden air stream passes to the membrane vapor separation system. A three stage membrane separation is required because the vent stream from the air stripper has a low VOC concentration. In the membrane vapor separation process, organic vapor-laden air contacts one side of a membrane that is permeable to organic vapors but relatively impermeable to air. The high permeability of the organic vapors is a result of the high level of sorption of the vapors into the membrane material. A partial vacuum, applied to the other side, draws the organic vapor through the membrane. The permeate vapor is then compressed and condensed to recover the organic fraction. The purified air stream is removed on the feed site, as the residue, and recirculated.

The goal of the program is to demonstrate that the two technologies can be combined successfully, while eliminating VOC emissions into the atmosphere. The combined system will be much smaller than a carbon adsorption system, more economical, and have none of the problems associated with spent activated carbon regeneration on-site or off-site. Pre-calculations indicate that the cost of air-stripper emissions treatment by membrane technology could be about $15/lb of VOC recovered, which is one-third or less of the cost of carbon adsorption treatment.

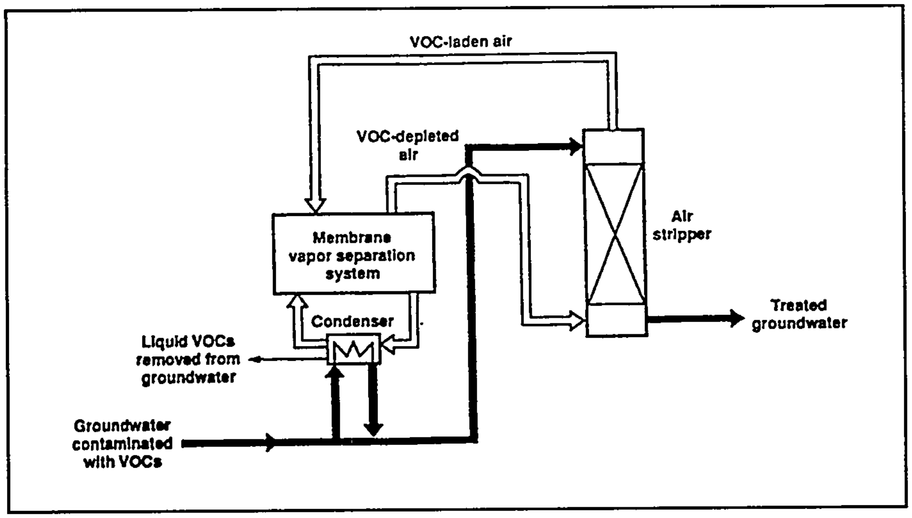

Figure 4.6. Simplified Flow Diagram of a Combined Air Stripper/Membrane Vapor Separation System.

TECHNOLOGY NEEDS

Groundwater and soil contamination are problems at many DOE sites. The two most common organic contaminants are TCE and carbon tetrachloride (CTET). Air stripping is the least expensive method of removing these VOCs from polluted groundwater. However, increasingly stringent environmental regulations require that VOCs in the resulting air stripper vent stream be captured or destroyed before discharging the stream to the atmosphere. Carbon adsorption is widely used to capture the VOC contained in the air-stripper emissions but produces a secondary waste in the form of spent carbon.

ACCOMPLISHMENTS

- The combined air stripper/membrane vapor separation concept was demonstrated successfully in a pilot-scale experiment.
- In 30 out of 37 experiments, VOC removal of 90 percent or more was achieved over a range of 0.38 to 500 ppm. A removal efficiency of 99 percent could be achieved with a taller air stripping tower.
- The cost of the combined air stripper/membrane vapor separation treatment is estimated to be about 6 cents per 1,000 gallons of treated groundwater.

COLLABORATION/TECHNOLOGY TRANSFER

The developer of this technology, Membrane Technology and Research, Inc., has applied the principles of membrane separation developed in this project to other DOE funded activities: Protective Clothing Based on Permselective Membrane and Carbon Adsorption (METC PRDA2), and Improved Membranes for Water Remediation Projects (Idaho PRDA).

The new technology can be used in two ways to improve VOC contaminated site remediation: (1) a complete combined system can be installed at the start of a remediation project, or (2) membrane vapor separation systems can be added to existing air strippers that are producing effluent air streams that do not comply with air-quality regulations.

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4.7 COMPOSTING OF SOILS/SEDIMENTS AND SLUDGES CONTAINING TOXIC ORGANICS, INCLUDING HIGH-ENERGY EXPLOSIVES

TASK DESCRIPTION

The objective of this project is to evaluate composting as a remediation technique for explosives found in the soils of DOE contaminated sites.

Composting is a biological process that utilizes the unique ability of thermophillic microorganisms to degrade toxic organics in soils, sediments, and sludges (see Figure 4.7). The compost environment is radically different from that found in aerobic soils and sediments because of the elevated temperatures and the variations in active microbial populations. This unique environment stimulates a variety of microbial enzymatic, chemical and thermal degradation reactions that would not occur under ambient conditions.

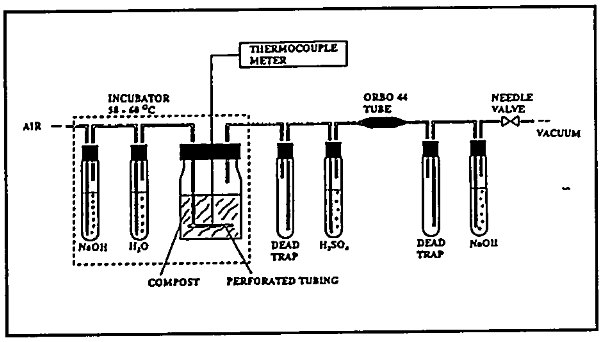

Figure 4.7. Laboratory-Scale Composting.

To perform the remediation, soils containing the toxic organics are mixed with nutrient and bulking agents and laid in a pile. The nutrients and bulking agents used can be any high organic-containing waste that is available locally. Typically animal manure, animal bedding, corn stalks, waste hay or straw, etc. are acceptable for use as nutrients or bulking agents. For hazardous waste composting, hot (60-65°-C), aerobic composts are used to facilitate the degradation of the toxic organics. In the field, this type of compost is achieved in forced-aerated windrows (long trapezoidal-shaped piles that are turned routinely and mechanically aerated).

In this study, experimentation will take place in three phases: (1) a survey of hazardous wastes present in soil and sediment at DOE's Pantex plant, (2) laboratory-scale composting of ^{14}C-labeled hazardous materials to determine the susceptibility of individual waste components to degradation by composting; the degradates produced and the mechanism of degradation; and the rate of soil loading tolerated by the compost, and (3) pilot-scale composting of soil contaminated with explosives to obtain realistic performance information and kinetic data.

TECHNOLOGY NEEDS

Soils contaminated with hazardous organic materials, including explosives, constitute a major problem at DOE's Pantex Plant. Incineration and landfill have been the major technologies utilized for soils that are highly contaminated with recalcitrant organics. Composting, with its unique biodegradation capabilities, is an alternative to incineration and landfill. In contrast with incineration, the resulting product is a fertile soil which can be returned to the original site or used elsewhere on the facility.

ACCOMPLISHMENTS

- Sixty-nine soil samples and one water sample were analyzed for the explosives TATB, PETN, RDX, and HMX. Levels of explosives were found to range from non-detectable to:

  * RDX - 66 µg/g
  * HMX - 109 µg/g
  * PETN - 201 µg/g
  * TATB - 349 µg/g

- Laboratory studies, conducted on ^{14}C-labeled explosives and ^{14}C-labeled diacetone alcohol contaminated soil loaded into horse manure/hay composts at three rates: 20, 30, and 40% soil loading levels, indicated that all explosives degraded rapidly and were reduced to below detection limits within 3 weeks.

- ^{14}C-degradates from ^{14}C-RDX, ^{14}C-HMX and ^{14}C-TATB were largely limited to $^{14}CO_2$. Volatile and non-volatile ^{14}C-degradates were found to result from ^{14}C-PETN breakdown. ^{14}C-diacetone alcohol concentrations were significantly reduced during composting.

- Data from pilot scale composts loaded with explosives contaminated soil at 30% soil loading levels with intermittent aeration, and monitored over six weeks, generally was in agreement with the laboratory studies. However, ^{14}C-labeled TATB degraded much faster than the unlabeled TATB. It is suspected that some formulations of TATB may be more resistant to composting activity than others.

COLLABORATION/TECHNOLOGY TRANSFER

A final report on the outcome of the experimentation activities was recently published. On the basis of data obtained from the pilot-scale studies, a demonstration plant was designed and estimated. Using four windrows, this demonstration plant would treat 55 cubic yards of explosives-contaminated soil. All of the pilot-scale composts were composted by day 42 to non-detectable levels for HMX (40 - 56 µg/g), RDX (54 - 88 µg/g), and PETN (68 - 88 µg/g) while 32 - 39 percent of the TATB was recovered (350 - 421 µg/g). Capital costs would be about $188,000, and operating costs would be about $409,000.

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4.8 DESIGN, MANUFACTURE AND EVALUATION OF A HYDRAULICALLY INSTALLED, MULTISAMPLING LYSIMETER

TASK DESCRIPTION

The purpose of this task is to develop a suction lysimeter that can be inserted into the vadose zone without using a predrilled hole and without incurring exorbitant costs.

Lysimeters are devices used to collect liquid samples from the vadose zone. The lysimeter sampling apparatus consists of a hollow porous section that is maintained at a vacuum. Liquid is transported into the lysimeter due to a pressure differential across the porous section. Liquid flow through the porous section is sustained by maintaining a pressure differential which is finite, yet below the air entry capillary pressure.

In this study, a new lysimeter will de designed that is comprised of a stainless steel ram point and body, one or more ceramic porous sections, and one or more extraction tubes (see Figure 4.8). The stainless steel ram point will be used for hydraulic or mechanical installation. This will eliminate the need to drill a well and reduce the risk of cross-contaminating soil horizons and the water table.

The effect of hydraulically inserting the lysimeter will be investigated by comparing the operation of the specially designed and constructed lysimeter that is manually driven into the soil with the operation of an identical lysimeter that is installed using standard procedures.

Tests that will be performed include bubble pressure, pore plugging, and soil moisture operating range tests. Visual inspections will be conducted to identify gross effects such as cracks, nonuniformity, and incorrect assembly.

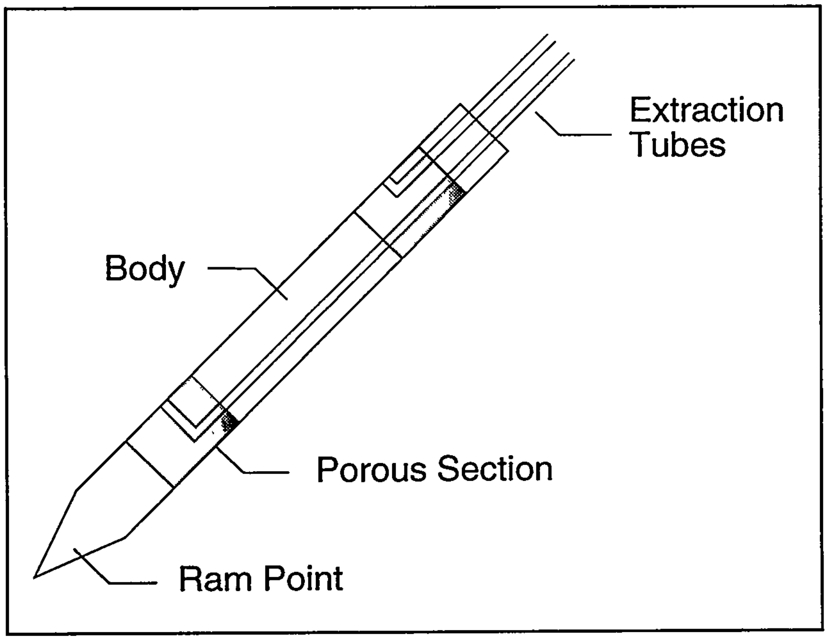

Figure 4.8. Schematic diagram of suction lysimeter.

TECHNOLOGY NEEDS

Chemical spills, underground storage tank leaks and improper burial of hazardous and toxic wastes can cause extensive groundwater contamination. Determining the extent of subsurface pollution and the potential for groundwater contamination requires vadose zone sampling and monitoring. Current subsurface characterization techniques are highly subjective and uncertain: A special need exists for three-dimensional characterization techniques. The multisampling lysimeter instrument might fill that need.

ACCOMPLISHMENTS

- The hydraulically installed suction lysimeter was capable of extracting soil pore liquid samples from unsaturated test soils without the need to predrill a well.
- More than 150 ml of pore liquid was extracted within a 24 hour period from test soils having less than 15 percent moisture content.
- Test results verified that the lysimeters installed with a hydraulic or mechanical ram were able to collect pore liquid samples in excess of the amount typically required for monitoring and analysis on a daily basis.
- Multiple sampling ports may be installed in an instrument to retrieve samples from multiple depths without sample contamination.
- Modifications to the prototype design eliminated moving parts and the need for inflatable packers. The elimination of the packer system and the case of porous nickel contributed to increased system ruggedness.
- Subsurface characterization using this technology will cost less than 20 percent of the cost to install a conventional cup lysimeter.

COLLABORATION/TECHNOLOGY TRANSFER

On the basis of test results, further development work will focus on improving the pore size distribution, strength of the porous ceramic sections, and on decreasing the overall diameter of the lysimeter to ease insertion and to conform to the standard size currently used in the cone penetrometer. Applied Research Associates, Inc., has developed technology to join site and subsurface exploration into a coherent program using the electric cone penetrometer (ECPT). The sampling port from the multi-sampling Blandon lysimeter can be really incorporated in the ECPT. Physical and chemical sensors can be readily integrated into the device.

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4.9

DEVELOPMENT OF A COMBINED SOIL-WASH/IN-FURNACE VITRIFICATION SYSTEM FOR SOIL REMEDIATION AT DOE SITES

TASK DESCRIPTION

The purpose of this task is to demonstrate the potential value of a remediation approach in which multiple technologies (soil washing vitrification) are integrated and multiple waste streams are blended.

Soil washing is a water-based, volume reduction process in which contaminants are extracted and concentrated into a small residual portion of the original volume using physical separation, and aggressive agitation and chemical extraction techniques (see Figure 4.9). The principal process involves transfer of the contaminants from the sediment to the wash water and their subsequent removal from the water. The small volume of contaminated residual concentrate is then treated by destructive or immobilizing processes.

Vitrification is a thermal process that converts materials into an alkali-boro-silicate glass or glassy substance. The process is conceptually attractive because of the thermodynamic stability of the product and the flexibility in treating a wide variety of waste streams and contaminants. In this study, the vitrification system uses a modified ceramic-lined melter with submerged inconel plate electrodes and relies on the conductivity of the molten glass to produce the joule heating effect (JHCM-Vitrification).

In this study, soil and sludges from the Weldon Spring, Missouri, site and storm sewer sediments from the Oak Ridge, Tennessee, site will be used for the testing of the system concept. Weldon Spring raffinate sludge will be included since this material due to the low silica content of the sludge and the insolubility of its contaminants which are distributed through the bulk of each particle rather than on the surface is not amenable to either soil washing or in-situ vitrification techniques. Oak Ridge Y-12 storm sewer sediments will be included since they are characterized by both a high silica fraction and a high contaminant content. The particular batch selected for this study averaged 4,000 ppm mercury, 630 ppm uranium, 1.2 ppm thorium, and 24 ppm PCBs.

TECHNOLOGY NEEDS

Contamination at DOE sites is widespread with contaminated soils and sediments estimated to total billions of cubic meters. Remediation technologies ultimately rest on some form of stabilization of the hazardous and radioactive contaminants into a solid, and therefore immobile, waste form that is stable and highly resistant to

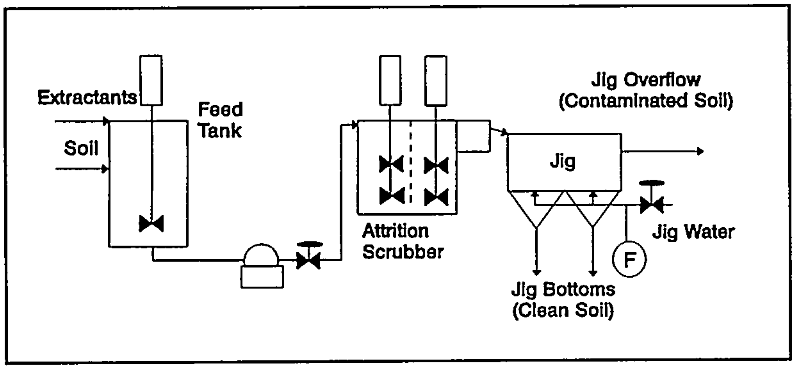

Figure 4.9. Schematic of Soil Washing Process.

aqueous corrosion and any other form of degradation. Central to an effective remediation system is the ability to concentrate the contaminants into the minimum possible volume since this reduces disposal and monitoring costs. The proposed integrated treatment system provides an alternative to solidification by cementation, which is usually perceived as an inexpensive option, but a far superior final waste form.

ACCOMPLISHMENTS

- Vitrification tests demonstrated that glasses having a high waste loading could be produced from the wastes at Weldon Spring.
- Raffinate sludges, due to their low silicate but high calcium, magnesium, and fluoride content could play the role of fluxes if appropriate blending schemes and glass composition formulations can be developed.
- Testing on the Oak Ridge material showed that both mercury and uranium could be removed from the sediment by soil washing techniques using chemical extraction, reducing the volume of the waste stream by 80 percent.
- For the contaminant-enriched minority fraction, thermal desorption was used to separate the mercury from the uranium, so as to produce a waste stream suitable for stabilization by vitrification.
- A system that combined soil washing, thermal desorption, and vitrification on Oak Ridge wastes produced clean soil (about 90% of the input waste stream), nonradioactive mercury, and a glass waste form.
- The estimated processing cost for such a system was in the range of $260 to $420 per ton of waste processed.

COLLABORATION/TECHNOLOGY TRANSFER

On the basis of these results, the integrated systems approach was incorporated in the Minimum Additive Waste Stabilization (MAWS) System for laboratory development and on-site demonstration at Fernald. The MAWS project began in June 1992, and on-site demonstration at Fernald began in mid-1993.

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4.10 DEVELOPMENT OF THE SEAMIST CONCEPT FOR SITE CHARACTERIZATION AND MONITORING

TASK DESCRIPTION

The purpose of this task is to develop the SEAMIST™ system for vadose zone gas and pore fluid sampling.

SEAMIST is a borehole liner and instrument emplacement technique that deploys an impermeable tubular membrane into a borehole by inversion under pneumatic pressure. The membrane supports the borehole wall and seals once it is emplaced, acting as low pressure liner. Instruments and sampling devices mounted on the membrane's surface are pressed against the borehole wall to maintain contact with the geologic media (see Figure 4.10).

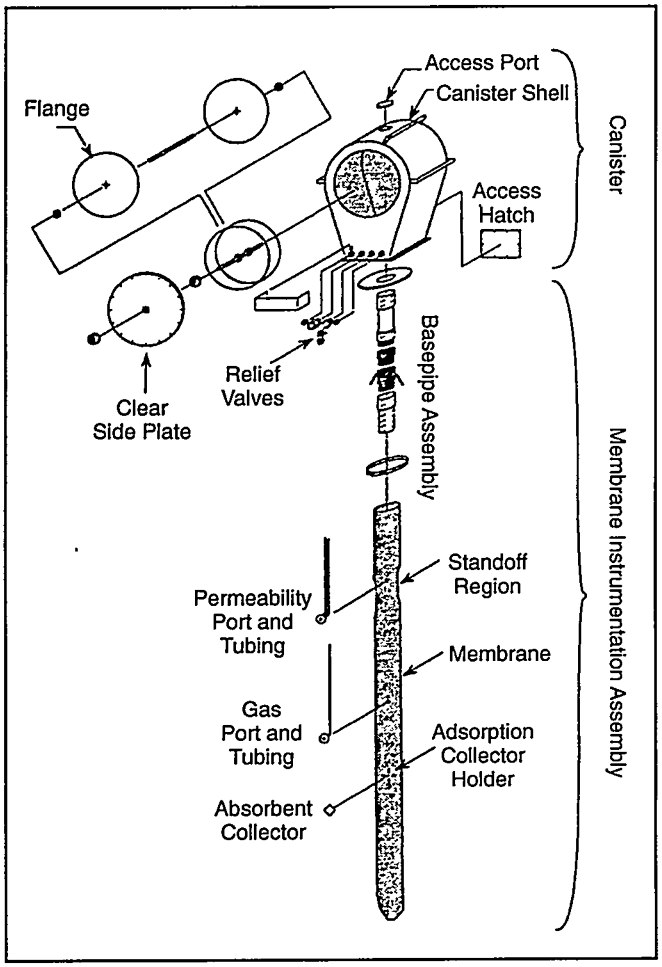

Figure 4.10. SEAMIST system components.

A significant capability of the SEAMIST system will be its ability to wick pore fluid from the unsaturated media with absorbent pads. The standard techniques using lysimeters cannot easily provide the frequency or degree of spatial resolution offered with the SEAMIST absorbent collectors.

The utility of the SEAMIST system therefore will lie in its rapid emplacement and high degree of spatial resolution attainable in the sampling systems. Emplacement rates of 10 to 20 ft/min would mean that most boreholes can be instrumented in less than 30 minutes, an improvement over current sampling systems which require several hours to a few days to become operational.

TECHNOLOGY NEEDS

Existing Federal and State regulations require knowledge of the distribution and behavior of contaminants in the subsurface environment to effectively characterize a site and/or monitor site cleanup activities. Conventional technologies rely on the construction of monitoring wells to characterize the nature and extent of vadose zone contamination.

The SEAMIST technique shows promise for use in in-situ instrument emplacement, emplacement of selective contaminant sampling devices, and transport of logging tools and cameras. As such, the method might provide better accuracy, higher spatial resolution, and less risk of contamination.

ACCOMPLISHMENTS

- The mechanical emplacement system was tested at the directional boring test range at Sandia National Laboratories.
- Field tests demonstrated the capability of the system in horizontal holes as long as 230 ft. Subsequent demonstrations were successful in vertical boreholes down to 130 ft.
- The membrane moved easily around corners and small obstructions in the borehole, and allowed repeated sampling in the same borehole over time to monitor contaminant movement.
- Systems were deployed in boreholes with diameters ranging from 1-3/4 in. to 10 in. with sampling instruments installed in less than 30 minutes, and absorbent collectors stationed at virtually any spacing.
- When the borehole was no longer needed, the membrane could be removed easily, without leaving behind residual material.

COLLABORATION/TECHNOLOGY TRANSFER

Based upon the experimental results, the technology was transferred to LLNL for monitoring of leachates and tritium in groundwater; to Sandia National Laboratory (SNL) for the lining of horizontal wells and sensor emplacement; to Savannah River Site (SRS) for dense non-aqueous phase liquids (DNAPL) characterization studies; and to Richland for soil gas monitoring.

In July 1993, the SEAMIST borehole instrumentation technology was sold to Eastman Cherrington Environmental, headquartered in Houston, Texas. Eastman Cherrington will be manufacturing and fielding the SEAMIST technology.

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4.11

ELECTROKINETIC TREATMENT OF CONTAMINATED SOILS, SLUDGES, AND LAGOONS

TASK DESCRIPTION

The main objective of this project is to investigate decontamination of soil by electrokinetic processes.

Electrokinetics is a relatively new remediation technology that uses low-level direct current on the order of mA/cm^2 of cross-sectional area between electrodes placed in the ground in an open flow arrangement (see Figure 4.11). This arrangement allows processing or pore fluid to flow into or out of the porous medium. The low-level direct current results in physico-chemical and hydrological changes in the soil mass, leading to species transport by coupled and uncoupled conduction phenomena.

To determine the feasibility of using electrokinetics to decontaminate soils, a number of electrokinetic tests lasting between 24 and 48 hours each will be conducted on various clay and clay-sand soil types impregnated with metals, surrogate radionuclides, and organic compounds prevalent at DOE sites. In the second phase, the electrokinetic process will be enhanced by physical methods (e.g., application of heat and high-frequency, low-amplitude seismic waves) and chemical methods (e.g., pH control, injection of complexing agents).

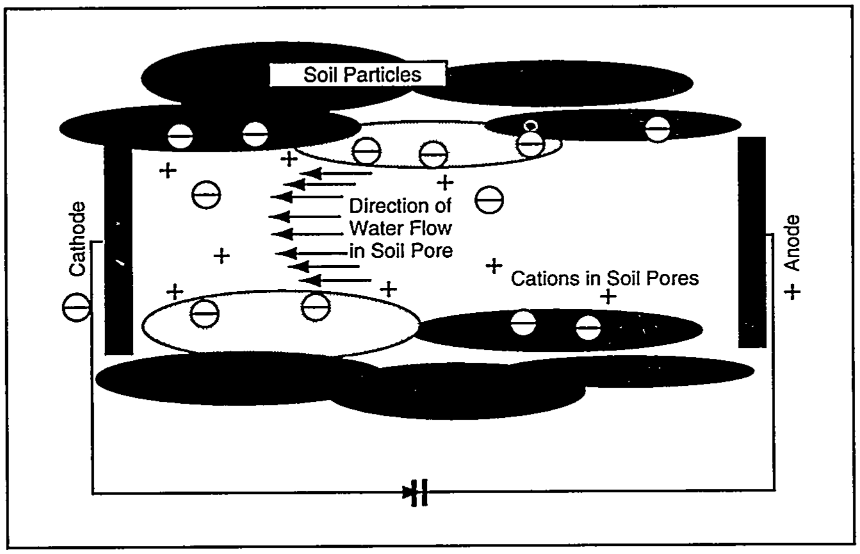

Figure 4.11. Schematic representation of electrokinetic process in soil.

To prepare the soil slurries used in these tests, an aqueous solution of the contaminants will be mixed with the soil, and the mixture will be consolidated into sample tubes. During these tests, systems will be monitored for voltage, current, and inflow and outflow of liquid through the soil. After the tests, soil samples will be analyzed for contaminants.

TECHNOLOGY NEEDS

Contamination by hazardous and radioactive materials in concentrated sediments and sludges exists at many DOE facilities. The migration potential of contaminants from waste sediments and sludges requires technologies to treat the contaminated volume in a manner that effectively protects the environment.

Technologies that provide cost-effective means for treating sediments and sludges in place or for efficiently removing them for treatment are needed. Electrokinetic processes could provide a significantly more efficient and cost effective means to effectively clean-up sites than other in-situ methods.

ACCOMPLISHMENTS

- Results from the tests indicate that electrokinetics can be an effective method of moving metal, radionuclides, and organics in both saturated and unsaturated soils.
- For constituents of an ionic nature, transport takes place by ion migration. For nonionic species, such as organics, the mobilization is by electroosmotic flow.
- In ion migration, electrochemistry of the species forced to migrate plays a predominant role whereas electroosmotic flushing is dependent on soil mineralogy.
- The process can remove up to 99+% of a number of metals, such as Cd, Ni, Zn, Pb. It was found that the pH, soil type, and metal type influence this removal.
- A simple empirical model predicts that for metals present at low concentrations or for poorly absorbed organics, electroosmotic flushing is the major transport mechanism.

COLLABORATION/TECHNOLOGY TRANSFER

The technology has potential for use in parallel with other remediation techniques such as pump-and-treat, bioremediation and vacuum extraction. When used in combination with electrical heating, the technology can be applied to remove polar and nonpolar chemicals from soil and groundwater. Based on the results of this study, the technology was transferred to SNL for removal of chromate contamination at the mixed waste landfill.

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4.12 FIBER OPTIC RAMAN SPECTROGRAPH FOR IN SITU ENVIRONMENTAL MONITORING

TASK DESCRIPTION

The objective of this project is to develop a powerful, field-size Raman spectrograph that can be used with a fiber-optic sampling probe for low detection of chemical species at the action levels required for remediation.

The experimental approach will focus on the fabrication of a "breadboard" version of a spectrograph/monochrometer that has high resolution and also covers the entire Raman spectral range. This will be accomplished by integrating a commercially available 52.65 groove/mm echelle grating, operated at an incident angle of 63.4 degrees, with a secondary dispersion element (a dual prism system) that allows the Raman spectrum (200-4,000 cm^{-1}) to be obtained in about 14 orders. A commercial software package will manipulate and store spectral information and maintain a database of spectra, which can be used with spectral matching algorithms

The result will be an instrument which contains no internal moving parts, and which is designed to have both a low f/# (high light collection efficiency) and small size, without sacrificing resolution (see Figure 4.12a). Optics will be matched to a fiber-optic input and 1:1 imaging at the focal plane. This fact combined with the exceptional sensitivity of a new generation of computer-aided design (CAD) detector arrays, means that low power laser sources can be used for conducting Raman spectroscopy.

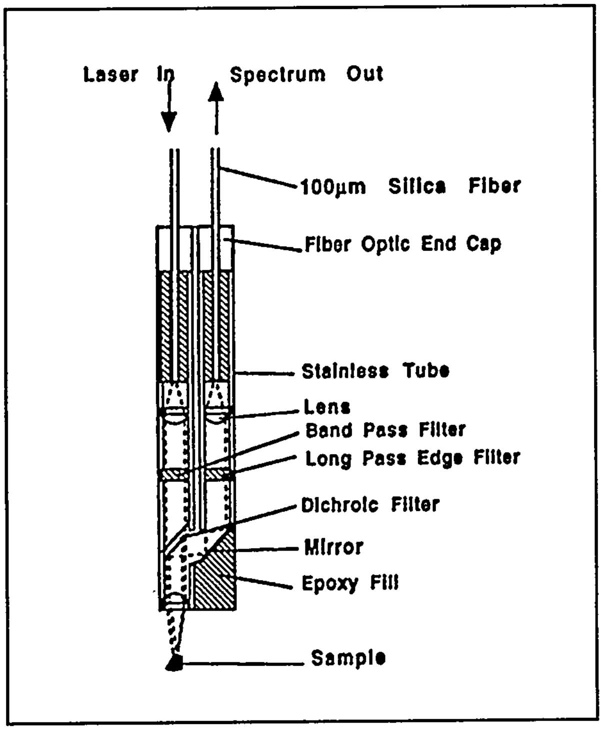

Figure 4.12a. Illustration of fiber-optic raman probe.

TECHNOLOGY NEEDS

Site clean up operations require on-line or rapid monitoring of the progress of the remediation process. Conventional sampling and analyses approaches rely on expensive and time consuming laboratory analysis of environmental samples. Real-time field analytical methods and technologies are needed to expedite this process and provide decision quality results, so as to ascertain the efficiency of site remediation efforts. In addition, more rapid and specific chemical characterization of a site will permit remediation activities to occur at a faster pace and to be aimed only at contaminated locations.

ACCOMPLISHMENTS

- Completed development of a prototype spectrograph that is 10 times more powerful than conventional Raman instruments, but one-tenth their size (see Figure 4.12b).
- New spectrograph features an optical throughput more than 10 times greater than that of existing Raman spectrographs.
- New spectrograph has a unique design that combines compactness and high light-collection efficiency without sacrificing resolution.
- Fiber-Optic Raman Spectrograph allows specific chemical characterization and, mapping within containers.

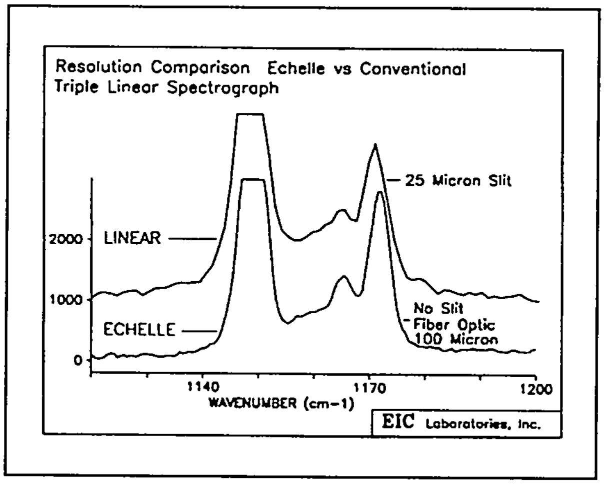

Figure 4.12a. Comparison of the EIC Compact Fiber-Optic Raman Echelle Spectograph for in situ monitoring and a conventional spexs triplemate. The Raman sample is naphthalene and the laser power was 100 mW.

COLLABORATION/TECHNOLOGY TRANSFER

EIC Laboratories, Inc., and Oak Ridge National Laboratories established a Collaborative Research and Development Agreement to exchange the technology and facilities necessary to develop and test this new fiber-optic Raman spectroscopy. EIC expanded the program to fabricate fiber-optic probes for testing of high-density contaminants at the Los Alamos mock-up waste storage tank. A later demonstration is planned for the Hanford Site.

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4.13

HIGH-RESOLUTION SHEAR WAVE REFLECTION SURVEYING FOR HYDROGEOLOGICAL INVESTIGATIONS

TASK DESCRIPTION

The main objective of this research is to develop the technology necessary to make high resolution shear wave (S-wave) profiling a useful tool in conducting shallow groundwater investigations.

Conventional seismic reflection utilizes elastic wave propagation to characterize the subsurface. Wave velocities depend upon mechanical and physical parameters, such as wave frequencies, fluid densities, bulk compress-ibilities (see Figure 4.13). Relationships between wave velocities and these parameters can be approximated, and these approximations correspond to the limit velocities of the compressional or P-waves and the shear or S-waves.

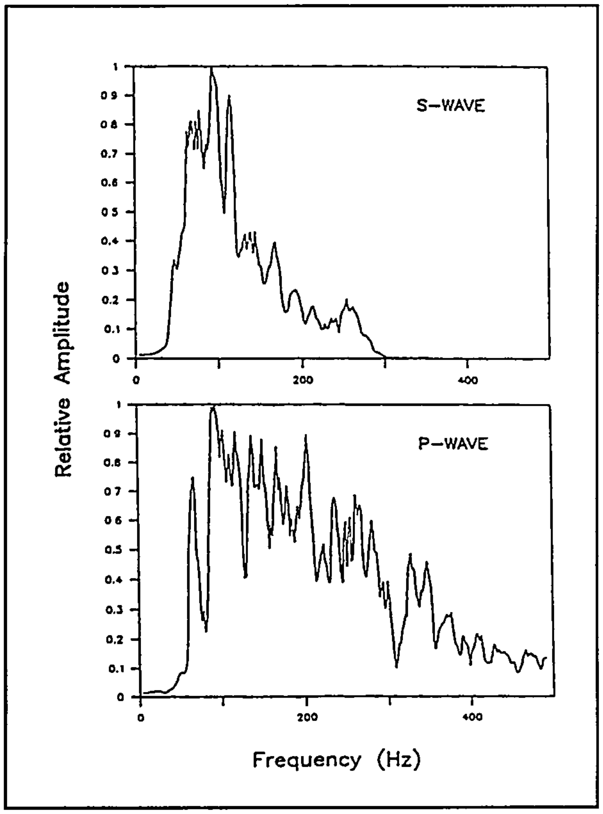

Figure 4.13. Amplitude spectra of P- and S-wave reflection signals.

Several characteristics of P- and S-waves make them potentially useful for characterizing shallow groundwater conditions. (1) S-wave velocities are severely affected if an unconsolidated sediment is saturated with water. The opposite is true with P-wave velocities. (2) The ratio of P-wave to S-wave velocity (V_p/V_s) can be an indicator of lithology. (3) S-waves are much more susceptible to the effects of anisotropy than are P-waves.

It is therefore anticipated that knowledge of S-wave velocities represents a powerful tool for assessing the fluid characteristics of subsurface layers, especially when combined with knowledge of P-wave velocities. Material properties (and lateral changes in material properties, such as a change from clay to sand) can be inferred from a careful, comparative evaluation of P-wave and S-wave records.

TECHNOLOGY NEEDS

Subsurface characterization, especially as it relates to groundwater flow, is a critical aspect of nearly all environmental restoration and waste management problems at DOE sites. Knowledge of detailed stratigraphic and aquifer conditions with minimal borehole control has the potential to have several positive impacts in characterizing a site.

ACCOMPLISHMENTS

- The theoretical basis of the research was tested at a field experiment at Cooke crossroads, South Carolina.
- Off-the-shelf equipment, commonly used for engineering geophysical applications, was used for P- and S-wave generation and recording.
- The S-wave reflection profile had more than double the resolution obtained with evaluation P-wave reflection under similar recording conditions.
- S-wave propagation added the detection and mapping of subsurface horizons as thin as one foot.
- Differences between P-wave and S-wave profiles could be related to the hydrogeologic conditions of the subsurface.

COLLABORATION/TECHNOLOGY TRANSFER

On the basis of the results obtained from the Cooke Crossroads test, the technology was transferred to the Savannah River Site. Here, the technology entered the Demonstration, Testing and Evaluation phase as part of the VOCs in Non-Arid Soils Integrated Demonstration on the characterization of DNAPLs. This experiment has recently been completed and the final results are awaiting publication.

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4.14 MINIMALLY INVASIVE THREE-DIMENSIONAL SITE CHARACTERIZATION

TASK DESCRIPTION

The objective of this project is to develop a synergistic approach to site characterization that avoids the performance deficiencies of the standard drilling and sampling method.

The Minimally Invasive Three-Dimensional Site Characterization (MISC) System uses a relational database management system to join site surface and subsurface exploration into a coherent program. Data and analysis results from Electric Core Penetrometer Test (ECPT) and from on-going surface geophysical surveys are transferred to on-site workstations where they are entered into a database/data modeling/data visualization program. Statistical analysis, site modeling, and data visualization are performed wherein all data sources are compared for identification of anomalous results.

The electric cone penetrometer hydraulically pushes a 1.405-in diameter instrumented rod into the ground to make geophysical measurements (see Figure 4.14). In addition to the standard subsurface characterization data, the ECPT also obtains downhole geophysical data that is used in the analysis of the surface geophysical survey. The methods chosen for the surface geophysical surveys are seismic profiling and electrical resistivity. Seismic reflection detects seismic impedance contracts which can identify hydrogeologic features. Resistivity is sensitive to providing effective profile measurements, such as contaminants in ground-water.

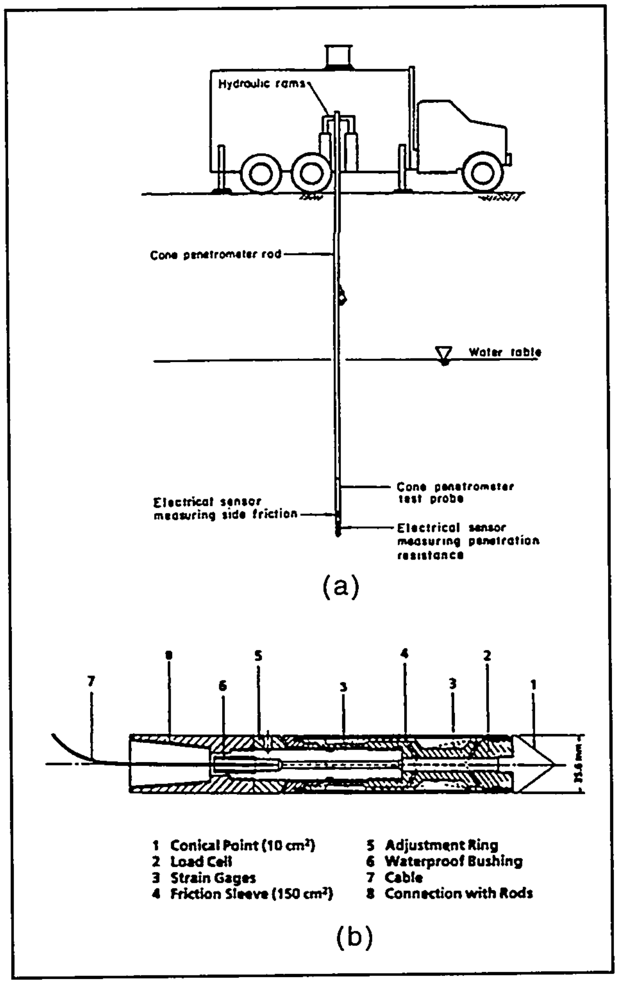

Figure 4.14. Cone Penetrometry: (a) typical cone penetrometer test rig; (b) electric friction-cone penetrometer tip.

By combining the results of fully coordinated surface and subsurface exploration activities, the expanded complementary database provides an increased understanding of the site hydrogeologic setting. In addition, observations are used to reduce the degrees-of-freedom in further geophysical inversions. The latter will result in optimum placement of monitoring wells, reduce the potential for site personnel to be exposed to hazardous materials, and minimize the hazardous material disposal problem associated with the exploration process.

TECHNOLOGY NEEDS

Characterization of subsurface stratigraphy and the nature of existing contamination is a fundamental step in every environmental site cleanup program. The current standard procedure for site characterization involves surface geophysics, drilling, sampling, laboratory testing, and placement of monitoring wells. This process suffers from a number of drawbacks: it is slow and expensive, it produces contaminated waste which must be disposed of, and its lack of interactive data analysis often results in an inaccurate interpretation of subsurface conditions. The MISC system allows data to be interpreted more fully and may provide for faster, cheaper, safer, and more accurate site characterization.

ACCOMPLISHMENTS

- This technology was tested at three sites: the Bethel-Royalton landfill in Vermont, the Los Lunas Volcano in New Mexico, and the Homestake Partners uranium mill site, in New Mexico.
- Performance Summary Development Testing at these sites confirmed the complementary nature of surface geophysics and electric cone penetrometer testing for site characterization.
- The data visualization capabilities afforded by the database/graphics program enhance the information learned from the survey data.

COLLABORATION/TECHNOLOGY TRANSFER

On the basis of the results, the developer of this technology (Applied Research Associates) has applied this technology to the integrated demonstration sites at the Savannah River Site (VOCs Non-Arid Soils Integrated Demonstration) and conducted several full demonstrations of the system.

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4.15 PREDICTED PERFORMANCE OF SYSTEMS FOR BULK SOIL ASSAY BARREL INSPECTION AND DECOMMISSIONING

TASK DESCRIPTION

The purpose of this project is to evaluate the applicability of new neutron interrogation systems designed to detect pollutants of concern for bulk soil assay, barrel inspection and decommissioning.

The experimental approach focuses on the use of Neutron Diagnostic Probe technology which is based on the AP TOF technique. The key component required for practical use of the AP TOF technique is a small sealed-tube neutron generator (STNG) that incorporates a position-sensitive alpha detector used to sense the alpha particle associated with emission of a 14-MeV neutron in the D (n, alpha) T reaction.

In operation, the STNG irradiates a large sample of soil with 14-MeV neutrons. Some of these neutrons interact with nuclei in the soil to produce inelastic gamma-rays, others are slowed down to thermal energy and interact with nuclei in the soil to produce capture-gamma-rays. The energy spectra of these two gamma-ray signals, together with the energy spectra from STNG operation in passive mode, in which the neutron generator is turned off, are used to identify elements in the soil and to estimate their concentrations.

The experimental effort of this project addresses the measurement of these gamma-ray signals using a laboratory system with a soil target containing known amounts of pollutants. The measured response to a known amount of pollutant is used to calculate the minimum detectable level (MDL) of that pollutant. The MDLs are then used to predict the performance of a Bulk Soil Assay system, a Barrel Inspection system to verify or determine the contents of 55-gallon barrels, and a facility decommissioning system.

TECHNOLOGY NEEDS

Many DOE sites are contaminated by radionuclides and heavy metals. These contaminants, embedded in structures, stored in 55-gallon drums and dispersed throughout the surface and subsurface, pose both chemical and radiological hazards that must be adequately characterized before selection of permanent disposal methods. The proposed neutron interrogation systems provide a non-invasive technology for contaminant screening for radio-nuclides. As such, they complement rather than compete with active and passive neutron detection systems developed to assay uranium and transuranics for nuclear safeguard applications.

ACCOMPLISHMENTS

- The STNG makes possible a unique Inelastic-Gamma Imaging and Spectroscopy (IGRIS), Capture-Gamma Ray Spectroscopy (CGRS), and Passive (STNG off) Gamma-Ray Spectroscopy (PGRS) system which provides a coarse three-dimensional image of the densities of elements in a target.
- Measurements, in measurement times of about 10,000 seconds (see Table 4.15), can be carried out simultaneously and are

complementary and synergistic with other technologies. System geometries were identified for Bulk Soil Assay, Barrel Inspection and Decommissioning of a facility.

- The Bulk Soil Assay system consists primarily of an IGRIS system. Complementary CGRS and PGRS measurements may be used if the IGRIS spectrum is too complex to be readily interpreted.
- The Barrel Inspection system is similar to the Bulk Soil Assay system. The imaging capability of IGRIS is used to detect pollutants concentrated in small volumes (voxels) that could be missed by chemical sampling techniques.
- The Decommissioning system is simply an IGRIS system designed to non-invasely detect a few grams of pollutants deposited in pipes, valves, etc., in measurement times of about 14 minutes.

Element/ Isotope	Mode	MDL Homogeneous Target	MDL Target in One Voxel
Bulk Soil Assay System			
Cs-137	PGRS	0.0078 pCi/g	2.5 nCi[a]
U-235	CGRS	11 ppm	3 g[a]
Cr	IGRIS	232 ppm	3 g[a]
Barrel Inspection System			
Cs-137	PGRS	0.0091 pCi/g	1.8 nCi[b]
U-235	CGRS	13 ppm	2.5 g[b]
Cr	IGRIS	270 ppm	2.2 g[b]

[a] Weight of voxel: 0.5 kg.

[b] Weight of voxel: 0.3 kg.

Table 4.15. Examples of predicted mininum detectable levels for proposed systems.

COLLABORATION/TECHNOLOGY TRANSFER

The STNG and IGRIS systems have been developed for detecting explosives and drugs concealed in containers and are being commercialized by Nuclear Diagnostic Systems. For environmental restoration applications, all three systems appear to have high payoff cost ratios. For non-radioactive pollutants, such as Hg and Pb, there currently is no effective non-invasive or non-destructive technology and the system tested might be the only alternative to scraping out samples and sending them to a laboratory for chemical analysis. Production costs for the Bulk Soil Assay and Barrel Inspection systems are expected to be less than about $500,000, while for the Decommisioning system cost is estimated at about $250,000.

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4.16 REMEDIATION OF GROUNDWATER CONTAINING RADIONUCLIDES AND HEAVY METAL USING ION EXCHANGE AND THE ALGASORB BIOSORBENT SYSTEM

TASK DESCRIPTION

The goal of this project is to determine the effectiveness of the AlgaSORB/ion exchange treatment process for removing low concentrations of heavy metal ions from contaminated groundwater.

AlgaSORB is an immobilized algal biomass that has high affinity for heavy metal ions. In this study, the material will be packed into columns similar to commercial ion exchange resins. Groundwater contaminated with heavy metals will be passed through columns containing the resin, which absorbs the metal ions. The metals will then be stripped from the resin, producing a highly concentrated waste stream.

The selected absorbent resins will be screened and tested for their efficiency in binding metal ions, before being analyzed for metal ion content. The most promising will advance to full-fledged column studies. The groundwater samples will then be pumped into columns at various flow rates. Effluents will be collected in four bed-volume fractions and analyzed for metal ion content. Different loading and stripping flow rates will be tested to optimize binding and stripping protocols. Finally, adsorbents will be recycled to measure any signs of diminished capacity.

The AlgaSORB/ion exchange technology will be tested with four different groundwaters from three different sites: Savannah River, Richland, and the Oak Ridge Y-12 plant. The objective is to perform bench-scale treatability studies to establish treatment protocols and to optimize an AlgaSORB /ion exchange technology system to remove and recover toxic metal ions from these contaminated groundwaters.

TECHNOLOGY NEEDS

Groundwater at many of the DOE sites has been contaminated with radionuclides, heavy metals, and/or inorganic ions. Because of the migration potential of these contaminants, technologies are needed to treat the contaminated groundwater in a manner that effectively protects the environment and human populations.

Candidate technologies for remediating groundwater containing radionuclides, heavy metals, and/or inorganic ions include: chemical treatment methods, and biological treatment methods.

The proposed system combines the benefits of both. Compared to ion exchange resins, an advantage of the immobilized algal biomass resins is that they are capable of producing effluent metal ion concentrations in the low part per billion range, even in the presence of high concentrations of hardness salts, such as those of calcium or magnesium.

ACCOMPLISHMENTS

- Treatability studies indicated that the specialty ion exchange/AlgaSORB resins tested in these studies show promise for selectively removing chromium, mercury and uranium from contaminated groundwaters at DOE sites.
- Over 4700 bed volumes of waters from Savannah River Well TBG-4 containing mercury at 10 ppb were treated producing effluents of less than 2 ppb mercury.

- Over 3000 bed volumes of waters from Well 399-1-117 containing uranium at 160 ppb were treated and produced effluents containing less than 10 ppb of uranium (see Table 4.16). For groundwaters from Well 199-H-4-14, over 1100 bed volumes of waters containing 323 ppb of chromium produced effluents containing less than 50 ppb of chromium.
- Over 2000 bed volumes of waters from Oak Ridge Building 9201-2 sumps in the Y-12 area containing mercury at 30 ppb were tested which produced effluents containing less than 2 ppb of mercury.
- The bounds of operating costs for a 600 gpm base system are $0.31/1000 gallon for chromium and $3.69/1000 gallon for mercury.

COLLABORATION/TECHNOLOGY TRANSFER

The AlgaSORB /ion exchange process is a technology that is aimed toward heavy metal ion treatment. Currently, systems that are capable of treating flow rates from as little as one gallon per minute up to several hundred gallons per minute have been manufactured and installed. One such system installed to treat contaminated groundwater in Michigan is treating a flow rate of 120 gpm to remove and separate chromium and nickel from the waters. The separated metals are then sent to a stainless steel manufacturer for recycling. It is not possible to specify the frequency of regeneration at this point in time. Assuming a typical rate of about one ounce per day, resin replacement needs to occur about every three years.

Adsorbent	Matrix	pH	Percent U Bound
AZ-601[a]	25 ppm U, DI water	5.0	99.5
AZ-602[b]	160 ppb U, Hanford water	5.0	26.5
AZ-316P[c]	160 ppb U, Hanford water	4.0	99.2
AZ-505[d]	160 ppb U, Hanford water	4.0	85.0
AZ-106L[d]	160 ppb U, Hanford water	7.7	88.0
AZ-423[d]	160 ppb U, Hanford water	7.7	88.0
AZ-320[d]	160 ppb U, Hanford water	7.7	99.1
AZ-320[e]	25 ppm U, DI water	7.7	98.0
AZ-423[f]	10 ppm U, spiked in Hanford water	7.1	99.7

Table 4.16. Uranium Batch Binding Studies.

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4.17 COMPETITIVE AND MASS TRANSFER EFFECTS ON THE SORPTION AND DESORPTION OF CONTAMINANTS IN SOILS

TASK DESCRIPTION

The specific objectives of this project are:

- Systematic determination of multiple contaminant effects on soil-groundwater partitioning at equilibrium;
- Measurements of multiple contaminant effects on liquid phase thermodynamic activities;
- Measurement of the mass transfer rates for contaminant exchange in unsaturated soils; and
- Measurement of specific mass transfer properties of soil-pore water-soil vapor partitioning including effective diffusivities, tortuosity and multiple solute diffusion coefficients.

Proposed studies will be carried out with three soil systems different composition selected on the basis of organic matter content and clay content. Multiple contaminant interactions to be studied with focus on mixtures of contaminants between classes. Thus mixtures of benzene, toluene, xylene (BTX) with chlorinated aliphatic contaminants will be investigated.

The basic experimental design is to compare observations carried out on single solute systems to the effects observed with binary and multiple contaminant systems (see Figure 4.17). Focus during the project renewal will be on contaminant interactions between contaminant classes (e.g., chlorinated solvents or BTX) on the basis of frequently observed combinations at field sites.

Development of equilibrium and mass transfer data will be carried out using incrementally more complex experimental designs. Initial studies will be carried out using sealed serum bottle equilibrium studies. Liquid phase thermodynamic activities for multiple contaminant systems will be determined based on liquid-vapor partitioning experiments.

Finally, diffusive transport of contaminants through unsaturated soils will be measured using the diffusion column apparatus developed during the first project period. Effective diffusion coefficients, effective tortuosity and soil-vapor partition functions will be determined as a function contaminant matrix, soil moisture content and soil type.

Quantification of organic species will be carried out using state-of-the-art gas chromatography or gas chromatography-mass spectroscopy techniques.

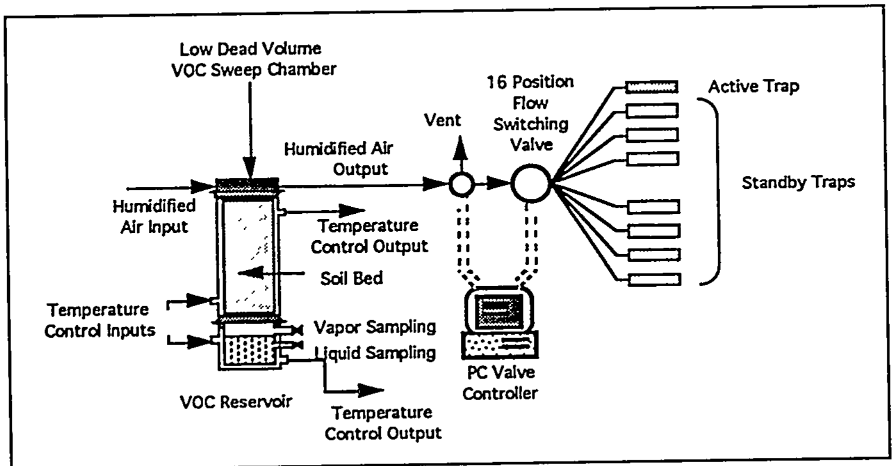

Figure 4.17. Diffusion apparatus for sorption and desorption of VOCs in soils.

TECHNOLOGY NEEDS

Remediation of contaminated soil and groundwater at hazardous waste sites is usually a predominant concern. Site characterization and monitoring is most frequently accomplished through sampling and analysis of groundwater. Subsequent states of the system are analyzed primarily on the basis of groundwater and soil vapor contaminant concentrations. This approach assumes readily predictable partitioning, both sorption and desorption, of contaminants between the aquifer (soil) and groundwater (aqueous) or soil, pore water and vapor phases. This dependence on accurate contaminant partitioning data becomes increasingly more acute as contaminant transport is modelled, and subsequently, for site remediation. Almost all in-situ remediation techniques rely on a sound understanding of contaminant partitioning, including equilibrium and mass transfer effects.

Currently, the overwhelming majority of contaminant partitioning data available is for single contaminant equilibrium with soil systems. However, most soil and groundwater contamination at hazardous waste sites consists of mixtures of organic contaminants. Multi-contaminant partitioning behavior is sought to be studied in this research project. Results are expected to provide fundamental data and models useful for carrying out site characterization, monitoring and in-situ remediation.

ACCOMPLISHMENTS

- Trichloroethylene diffusion through Quakertown silt loam soil at different moisture content was evaluated. Data were examined to determine the effects of soil moisture on VOC diffusion behaviors.
- A mathematical model of the diffusion process through soil was developed from shell mass balances on the diffusing solute for both the interparticle and intraparticle systems.
- An apparatus for experimental measurement of VOC diffusion in unsaturated soils was designed and constructed.
- Better VOC sampling and GC/MS analytical techniques were developed to provide the ability to collect samples over broad VOC concentration ranges without overloading the traps and GC/MS.

COLLABORATION/TECHNOLOGY TRANSFER

This research is carried out in a collaborative effort between the EPA, DOE and Rutgers University.

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4.18

DEGRADATION OF CHLORINATED ALIPHATIC COMPOUNDS BY AUTOTROPHIC NITRIFYING BACTERIA

TASK DESCRIPTION

While various microbial processes may be available to degrade chlorinated aliphatic compounds, considerable research has focused upon the use of organisms containing monooxygenase and dioxygenase enzymes. These organisms enzymatically degrade chlorinated aliphatic compounds through oxidative dehalogenation which has been demonstrated for mixed and pure cultures grown on toluene and ammonia. The pathways used by these organisms involve a cometabolic process of reductive-dependent oxidation of the chlorinated aliphatic compounds.

Of these three bacterial types, this proposal will focus on the autotrophic ammonia-oxidizing bacteria, of Nitrosomonas organisms. These organisms were chosen because of a general lack of knowledge about oxidative dehalogenation with the nitrifiers as compared to either the methanotrophs or toluene-degraders. Several characteristics of the nitrifiers are attractive for bioremediation and for fundamental studies of oxidative dehalogenation. The ubiquitous presence of nitrifiers in natural soil environments makes these organisms of particular interest to in-situ bioremediation processes. Their activity can be stimulated by the addition of ammonia and oxygen. In addition, experimentation in the laboratory with these organisms is relatively simple. The low cell growth rates allow the determination of substrate utilization rates under a variety of experimental conditions without significant changes in cell concentrations due to growth. Substrate utilization rates can be easily measured as either the consumptions of ammonia or oxygen, or the production of nitrite, all of which can be done nearly continuously.

The objectives of this research are as follows:

1. Comparison of Chlorinated Aliphatic Degradation Rates for Nitrifiers to Methanotrophs

Through the use of kinetic models, substrate and co-substrate utilization rates will be measured and used to describe the potential of nitrifying bacteria to oxidize a variety of chlorinated aliphatics.

2. Assess Physiological Response to Co-metabolic Toxicity

The second objective is to determine the factors which allow cells with toxic effects resulting from the co-metabolism to undergo self-regeneration of cellular components required to sustain co-metabolic activity. These metabolic effects include the depletion of energy reserves, prolonged reductant deprivation, and inactivation of cellular components by co-metabolic reaction products.

3. Development of Optimum Reactor Design for Co-metabolic Degradation Using Nitrifiers

The objective would be to compare different reactor designs to determine the optimal configuration for nitrifying organisms using the results from Objective 1 and 2. Reactor types to be examined would be plug-flow versus completely-mixed, suspended versus attached growth, steady-state versus non-steady state influents with respect to substrate, and steady-state versus non-steady state influents with respect to the co-substrate.

TECHNOLOGY NEEDS

A variety of aliphatic chlorinated compounds are commonly found in hazardous waste sites and contaminated groundwater. Many of these compounds are important because of their large production rates and potential adverse environmental effects. Specific examples include trihalomethanes, vinyl chloride, dichloroethylene, trichloroethylene, tetrachloroethylene, di-chloroethane, and trichloroethane. They can have high carcinogenic potency factors and/or other toxicity and are often degraded at slow rates. This makes such compounds of particular interest for site remediation involving either pump-and-treat or in-situ technologies.

Of the potential treatment methods, bioremediation is an attractive alternative for contaminated aquifers. Biological treatment can result in complete degradation which, in some instances, can be accomplished in-situ. Preliminary cost estimates suggest that bioremediation will be less expensive for contaminated soils than alternative treatment methods such as incineration or removal to landfills. Bioremediation, however, is currently not readily accepted by the engineering community because of a lack of both fundamental understanding and field experience. There exists a need for additional research to improve fundamental understanding and to provide optimal engineering designs.

ACCOMPLISHMENTS

- Substrate and cosubstrate degradation rates were studied. Results demonstrated that there is a very rapid inhibition of ammonia oxidizing activity immediately after addition of TCE. The rate of inactivation is also dependent on the TCE concentration.

- The rate of inactivation is largely independent of the ammonia concentration.

- Physiological response to toxicity was studied. The kinetics of recovery of ammonia oxidizing activity is a function of the degree of inactivation by TCE.

- Higher concentrations of TCE were shown to completely suppress protein synthesis during the period of exposure to TCE.

- A poster presentation was made at the Western Region HSRC annual meeting in July 1993.

COLLABORATION/TECHNOLOGY TRANSFER

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4.19

EFFECT OF NATURAL DYNAMIC CHANGES ON POLLUTANT-SEDIMENT INTERACTIONS

TASK DESCRIPTION

The overall objective of the proposed research is to determine the factors which control the slow release of contaminants from sediments and dredge materials. Initially, the kinetics of adsorption and release of hydrocarbons from a variety of sediments will be measured for hydrocarbons of widely differing polarity and hydrophobicity. These experiments will be done in sealed reaction vessels in the laboratory under carefully controlled and varied environmental conditions.

The initial batch experiments have been designed to address the fundamental question of adsorption/desorption hysteresis. This hysteresis or irreversibility is important to the fate of hydrocarbons in sediments and dredge materials. The chemicals to be used represent typical hazardous substances found in sediments in Regions 4 and 6. Batch adsorption/desorption experiments were designed to mimic of pollutant/sediment interactions in a river or lake environment. Priority pollutants with well-defined physical chemical properties were chosen as model pollutants. The sorbent used was sediments obtained from Johnson Ranch, Lula, Oklahoma, where the ranch is located near the margin of the flood plain of a small river.

TECHNOLOGY NEEDS

Sediments and dredge materials in EPA Regions 4 and 6 are often contaminated with hydrocarbons from different sources. Petroleum by-products from production, refining, and exhaust materials are often adsorbed onto solid sediments. A similar fate exists for waste products of wood treating and other industries in these geographic areas. Data are needed to predict the rate at which common sediment contaminants will be released either due to normal seasonal variations or during dredging operations. Laboratory screening of sediments, chemicals, and conditions proposed in this research project may provide the information sought. The knowledge gained may eventually aid the design of more realistic dynamic column experiments and a field test of contaminant sorption and release rates. Finally, measurements of the proposed kinetics and interpretation in terms of fundamental mechanisms should greatly improve our ability to predict and control the release of hazardous materials from sediments and dredge materials.

ACCOMPLISHMENTS

- The effect of various naturally fluctuating parameters on adsorption and desorption behavior of hydrocarbons has been determined using batch experiments.
- Some sediments and dredge materials have been exposed to the chemicals which are irreversibly bound.
- The binding increases with exposure time and the effect is more pronounced for the more hydrophobic chemicals.

COLLABORATION/TECHNOLOGY TRANSFER

This is a collaborative research project between the U.S. EPA, DOE and Rice University. Experiments in this research were designed and conducted in cooperation with Professors Hughes and Ward.

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4.20 ELECTROCHEMICAL SENSOR FOR HEAVY METALS IN GROUNDWATER: PHASE II-INSTRUMENT DEVELOPMENT AND FIELD DEMONSTRATION

TASK DESCRIPTION

This project's objective has been to develop and demonstrate a field portable instrument for real-time *in-situ* measurement of environmentally significant heavy metals in surface or ground water at part-per-thousand to ppb levels. In the first phase of this research, researchers have successfully constructed and tested the electroanalytical component of the sensor (see Figure 4.20), the mercury-coated iridium ultramicroelectrode (Hg/IrUME). It is capable of measuring heavy metal ions such as lead and cadmium, from low-ppb to high-ppm levels, in various model and natural water systems. Currently researchers are testing a truly novel and unique prototype IC-based twenty-element array version of the Hg/IrUME with increased sensitivity, reproducibility and stability.

During the proposed second phase of this research, researchers aim to incorporate a final version of this unique microarray sensor into a custom made portable instrument, test its operation in the laboratory under expected field conditions, identify demonstration sites in EPA Regions 1-2, develop appropriate test protocols and field test with split samples.

TECHNOLOGY NEEDS

A major portion of all drinking water either subsides or is transported as groundwater. Improved, low-cost, and timely on-site, in-situ characterizations are essential for site monitoring and remedial actions, for restoration of contaminated aquifers. Other detection methods currently in use are well suited for organics, gases, pH, etc., but are not suitable for priority heavy metals. In addition, analytical data turnaround for state, federal and commercial laboratories typically exceeds several months, resulting in increased costs and delayed decisions. On-site characterization for treatment and remediation would greatly benefit from the ability to rapidly monitor these and perhaps other environmentally significant toxic metals. This project addresses the enhancement of on-site, in-site screening and quantitative measurement of heavy metals in groundwater.

Electrochemical techniques, because of their remarkable sensitivity and ease of use in aquatic media, have offered the promise of being versa-

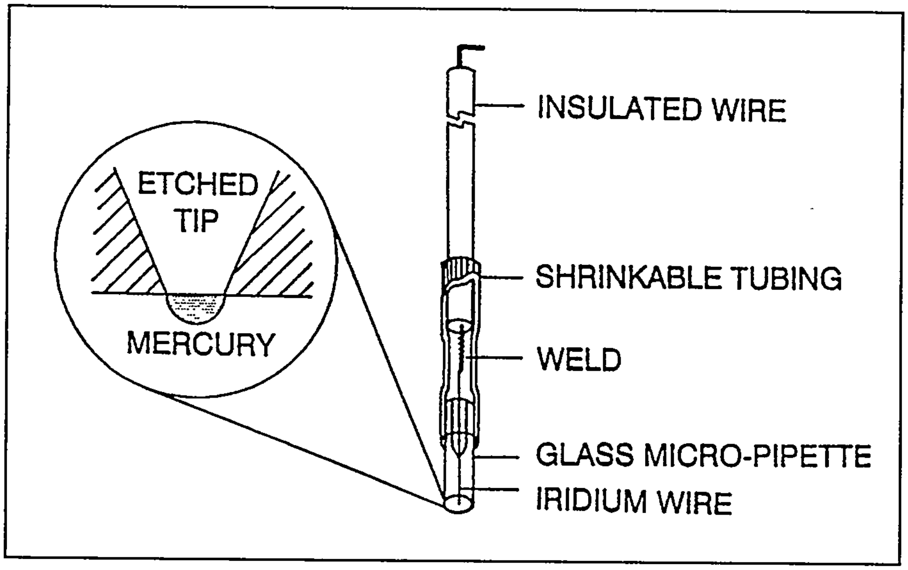

Figure 4.20. Schematic representation of the electrochemical sensor.

tile and efficient approaches for in situ measurement of metal-ion species.

ACCOMPLISHMENTS

- A prototype instrument using the array sensor operative with an external potentiostat has been assembled.
- The electrochemical operation of the instrument and its quantitative analytical capabilities with natural water samples were extensively evaluated. The results appear promising and only minor modifications will be required for the final version of the sensor.
- Two papers were submitted for publication.

COLLABORATION/TECHNOLOGY TRANSFER

A collaboration has recently been established between Tufts/Northeast HSRC and two other major research groups at the Center for Integrated Systems at Stanford University and EG&G Instruments at Princeton, NJ. The research is supported by funds from the EPA and DOE.

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4.21 ELECTROOSMOTIC PURGING OF HEAVY METALS AND MIXED HAZARDOUS WASTES FROM PARTIALLY AND FULLY SATURATED SOILS

TASK DESCRIPTION

The overall objective of the proposed research is to develop a comprehensive mathematical model for simulating the complex physiochemical and electrochemical interactions occurring in electrokinetic soil remediation as exemplified by the Massachusetts Institute of Technology process of electroosmotic purging. A supporting experimental program is planned to determine practical limits to soil permeability and saturation level, as well as to evaluate pH control options. The theoretical model is seen as a cost-effective tool for bridging the gap between the well-controlled laboratory environment and application of the technology in the field. It will serve to establish optimum operating conditions and to predict practical removal efficiencies on a site-specific basis. The model should also prove useful as a decision-making aid when assessing different remediation options.

In electrokinetic remediation, a voltage is applied across electrodes that are emplaced in the soil that is to be treated. The resulting electric field induces motion of the liquid, dissolved ions, and possibly colloid-sized particles suspended in the liquid. The contaminants are moved by three processes, namely electroosmosis, electromigration, and electrophoresis.

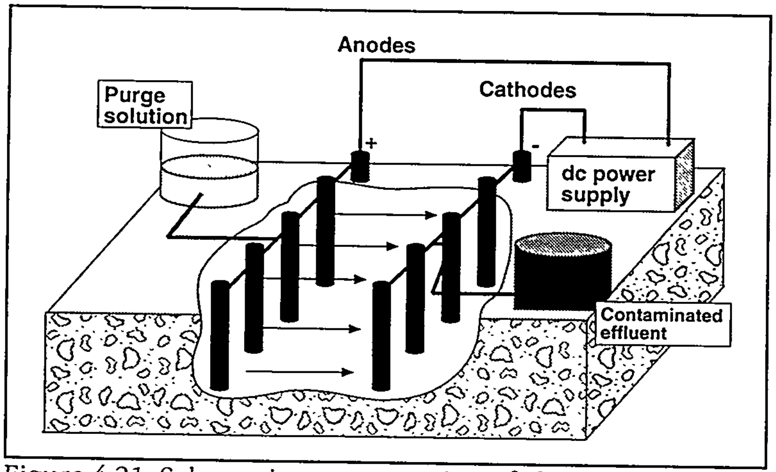

Figure 4.21. Schematic representation of electroosmotic purging of contaminated effluents.

The relative contribution of each mechanism — electroosmosis, electromigration, and electrophoresis — depends on the physical and chemical properties of the soil matrix, the contaminants, and the liquid. In cases where these processes are slow or concentration gradients are high, simple concentration diffusion may also affect the overall transport process.

In the electroosmotic purging process, a purge solution which is introduced at one of the electrodes serves to enhance the efficiency of the process.

TECHNOLOGY NEEDS

Hazardous wastes including radioactive and non-radioactive heavy metals, organic solvents, and hydrocarbons may have contaminated aquifers as a result of being leached from landfills or sludge ponds and even direct application of wastes to the soil. Sources of these contaminants include metal plating operations, fossil-fuel power plants, petroleum and chemical processing operations, nuclear weapons manufacture, and uranium enrichment operations.

The application of electrokinetic technologies to hazardous waste remediation is expected to produce a low cost, in-situ process for treating soils that are saturated or partially saturated with contaminated liquids.

This research has the potential to make available a new and important tool for in-situ decontamination of soil at many DOE sites.

ACCOMPLISHMENTS

- Laboratory experiments applying dc electric fields to soils containing aqueous solutions of soluble contaminants have been carried out. Results are encouraging and hold the promise of eventual development of effective in-situ means for cleaning waste sites.
- Limited field tests and computer modeling support the above projection.

COLLABORATION/TECHNOLOGY TRANSFER

This research project is funded by DOE and carried out at Massachusetts Institute of Technology.

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4.22 ENHANCEMENT OF BIODEGRADATION THROUGH THE USE OF SUBSTITUTED PORPHYRINS TO TREAT GROUNDWATER CONTAMINATED WITH HALOGENATED ALIPHATICS

TASK DESCRIPTION

The long-term objectives of the proposed research is the development of a process for the dehalogenation of halogenated hydrocarbons found to contaminate ground water at DOE sites. The proposed process will use porphyrins and porphyrin derivatives as catalysts for the reductive dehalogenation of halogenated compounds. In those cases where sufficient dehalogenation can be obtained to make the products amenable to ordinary biological waste treatment (activated sludge, for example), we envision that the proposed process would use a fixed or fluidized-bed reactor containing immobilized porphyrins. If only partial dehalogenation of some of the more heavily halogenated compounds is obtained, we envision the immobilized porphyrin reactor as a pretreatment system for specialized biological reactors such as methanotrophic or dehalogenating anaerobic cultures. These biological systems have been shown to dehalogenate a number of halogenated hydrocarbons; however, these systems work more efficiently with less halogenated substrates.

Specifically, the research objectives of this project will be as follows:

(1) Optimize dehalogenation reactions with respect to porphyrin structure, reductant, and reaction conditions. Identify reaction products from test compounds.

(2) Screen immobilization methods and optimize the activity of immobilized porphyrins. Evaluate reactor designs.

(3) Determine biotreatability of product mixtures in methanotrophic and anaerobic systems. Optimize and operate a continuous system augmented with porphyrins.

TECHNOLOGY NEEDS

Metal substituted porphyrins are organometallic molecules that can be used to catalyze the degradation of several classes of hazardous chemicals. This proposal presents a plan to develop and demonstrate the use of reduced metal porphyrins for catalytic pretreatment of chlorinated aliphatic pollutants in water treatment. Conceptually, treatment could occur (1)æabiotically in reactors containing immobilized porphyrins prior to biological treatment, or, (2)æin anaerobic microbial systems, including methanogenic ones, that have been augmented with porphyrins. Chlorinated aliphatic hydrocarbon compounds are frequently found contaminants in groundwater at many government and non-government sites. Conventional technology, such as activated carbon and air stripping only transfer the contaminants into another medium.

COLLABORATION/TECHNOLOGY TRANSFER

This proposal presents an integrated research project to be executed by ABB Environmental Services, Inc. (ABB-ES), University of Tulsa Center Environmental Research and Technology, and the Western Region Hazardous Substance Research Center at Stanford University (WRHSRC).

The three investigators will coordinate their efforts to optimize the catalytic activity of immobilized porphyrins in reductive dehalogenation and to efficiently interface these systems with the appropriate biological reactor. Close cooperation between the three groups and with other groups of the WRHSRC will be crucial for the success of this project. ABB will be the prime contractor to the WRHSRC with the University of Tulsa being a subcontractor to ABB. The project is funded by DOE.

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4.23

FACTORS LIMITING MICROBIAL DEGRADATION OF POLYNUCLEAR AROMATIC HYDROCARBONS

TASK DESCRIPTION

The work proposed in this project will delineate the biochemical reactions by which Polynuclear Aromatic Hydrocarbons (PAHs) may be degraded, and how these reactions are regulated in the presence of background organic compounds. The proposed work has the following objectives: to determine the metabolites that inhibit the degradation of higher molecular weight PAHs; to determine the metabolic mechanisms by which a selected laboratory strain is able to diminish the inhibition of PAH degradation that occurs when *Pseudomonas* sp. ANT-1 is presented with complex mixtures of PAHs; to isolate additional bacterial strains that degrade PAHs and determine the generality of the inhibition phenomenon observed with *Pseudomonas* sp. ANT-1; and to construct a hybrid bacterial strain that degrades PAHs present both singly and in mixtures, without inhibition of higher molecular weight compound degradation. An expected outcome from the proposed work will be the development of bioremediation approaches that will both accelerate the rate at which PAH degradation occurs, as well as the amount of degradation that may obtain. Such information should facilitate the optimization of technology that may be used for bioremediation of PAH-contaminated soils, either *in situ*, by composting, or in bioreactors.

Objectives of this work include:

1. Determine metabolites that inhibit degradation of larger molecular weight PAHs.

2. Determine the metabolic mechanism(s) by which the laboratory strain is able to diminish the inhibition of PAH degradation by our PAH degrading bacterial strain, *Pseudomonas* sp. ANT-1.

3. Isolate additional bacterial strains which degrade PAHs and determine the generality of the observations with bacterial strain, *Pseudomonas* sp. ANT-1.

4. Time and resources permitting, the researchers will construct a hybrid bacterial strain which degrades PAHs present both singly and in mixtures without inhibition of higher molecular weight compound degradation.

TECHNOLOGY NEEDS

Polynuclear aromatic hydrocarbon (PAH) compounds are widespread contaminants resulting from combustion processes, petrochemical spills, wood treatment facilities, and other industrial activities. Many of these compounds are genotoxic; hence in view of their ubiquitous distribution and potential for adverse effects on human health and environmental welfare, their removal is a high priority concern for regulatory agencies. Biodegradation of such compounds, however, is difficult, reflecting the physical properties of PAHs as well as the lack of understanding concerning the biochemical reactions and their regulation at the cellular level by which metabolism of such compounds may occur and subsequently be optimized.

ACCOMPLISHMENTS

- Demonstrated the influence of single PAH species on the degradation of other PAH species present singly or in combination.

- Several PAH degrading bacterial strains were isolated. Two of these isolates degrade significant concentrations of 2, 3 and 4 ring compounds.

- Biochemical tests of the isolates suggested that both belonged to Mycobacterium species.

- One of the isolates, strain ANT 2, exhibit good degradation of higher molecular weight compounds in mixtures as well as when substrates are present singly.

- Results have been published.

COLLABORATION/TECHNOLOGY TRANSFER

This work was done in collaboration with Howard University (Dr. James Johnson) and Michigan State University (Dr. James Tiedje), and sponsored by EPA and DOE.

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4.24

HEAVY METALS IN CERAMIC MATRIX: HEAVY METAL/CLAY INTERACTIONS IN CERAMIC PROCESSING

TASK DESCRIPTION

The goal of this research is to evaluate a method for rendering industrial waste sludges nonhazardous by incorporation of the sludge into a ceramic matrix (see Figure 4.24). The project is comprised of the following six tasks:

(1) Conduct a comprehensive literature search in the field of ceramic production methods and chemistry.

(2) Choose ranges in the major variables that are relevant to producing ceramic samples and production of ceramic pellets for preliminary evaluation.

(3) Evaluate criteria of the ceramic products from both a practical and scientific standpoint. Leaching criteria will be completed first. Next chemical analysis will be carried out. This will use Atomic Adsorption, Scanning Electron Microscopy, Photoelectron Spectroscopy and Extended X-Ray Absorption Fine Structure.

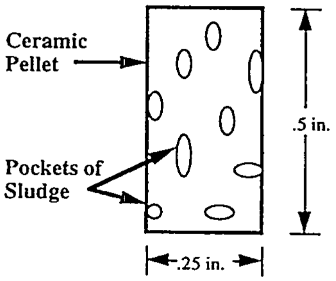
(4) Evaluate and refine the variables chosen in Task 2 so that optimal conditions for the ceramic product are chosen.

(5) Bench-scale production of the ceramic product using the optimal conditions chosen in Task 4.

(6) Evaluate various uses for the ceramic product such as an additive in cement.

There are several possibilities for the incorporation of sludge (metals) within the ceramic matrix:

1) Heterogeneous mix (large pockets of sludge within ceramic):



2) Homogeneous mix (well distributed sludge within matrix):

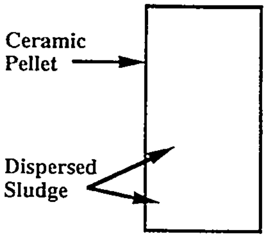


Figure 4.24. Metal incorporation into ceramic matrix.

TECHNOLOGY NEEDS

There are nontrivial reasons why most heavy metal sludge disposal processes have not been totally satisfactory. the problems arise from the fact that the contaminant element can only be changed in form but not destroyed. Thus, the engineered processes that are applied to processing heavy metals sludges must transform the heavy metals into a nonleachable material which has robust characteristics vis a vis the disposal environment, typically a landfill. The matrix of the processed material (concrete, glass, etc) must be able to withstand mild acidic conditions and natural sequestering agents. Often the landfill conditions also include reducing conditions sufficiently severe that sulfides and methane can be present. The proposed research addresses a prospective process that should lock heavy metals into a ceramic matrix sufficiently robust to withstand the rigorous conditions described above.

ACCOMPLISHMENTS

- A method was developed for producing a heavy metal sludge that can be experimentally reproduced.
- The method is used for producing heavy metal sludge.
- The production of a sludge containing 0.5% heavy metal is carried out by combining two separate sludge components.

COLLABORATION/TECHNOLOGY TRANSFER

The EPA, DOE and Stanford University have collaborated in this project.

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4.25 IN SITU BIOREMEDIATION OF CHLORINATED ALIPHATIC COMPOUNDS BY PHENOL UTILIZING BACTERIA

TASK DESCRIPTION

The goal of this project is to evaluate, in the field, the rate and extent of degradation of chlorinated aliphatic compounds through cometabolism using phenol as a primary substrate (Fig. 2.2.9.1).

Recent research has indicated that microorganisms containing the toluene monooxygenase (TMO) or toluene dioxygenase (TDO) enzyme can oxidize chlorinated aliphatic compounds such as tricholoroethylene (TCE) by cometabolism, similar to biodegradation by methanotrophs with methane monoxygenase (MMO). The toluene oxygenases can be induced by several primary substrates, including phenol. In order to obtain a comparison between the relative advantages and disadvantages of the TMO or TDO systems and the MMO enzyme system, an evaluation will be conducted at the field site at Moffett Field Naval Air Station in California.

The field study will be conducted in the same manner as the previous study in which methane was used as a primary substrate so that the results can be directly compared. Here, phenol and oxygen will be dissolved in recycled groundwater along with TCE, dichloroethylene (DCE), and vinyl chloride

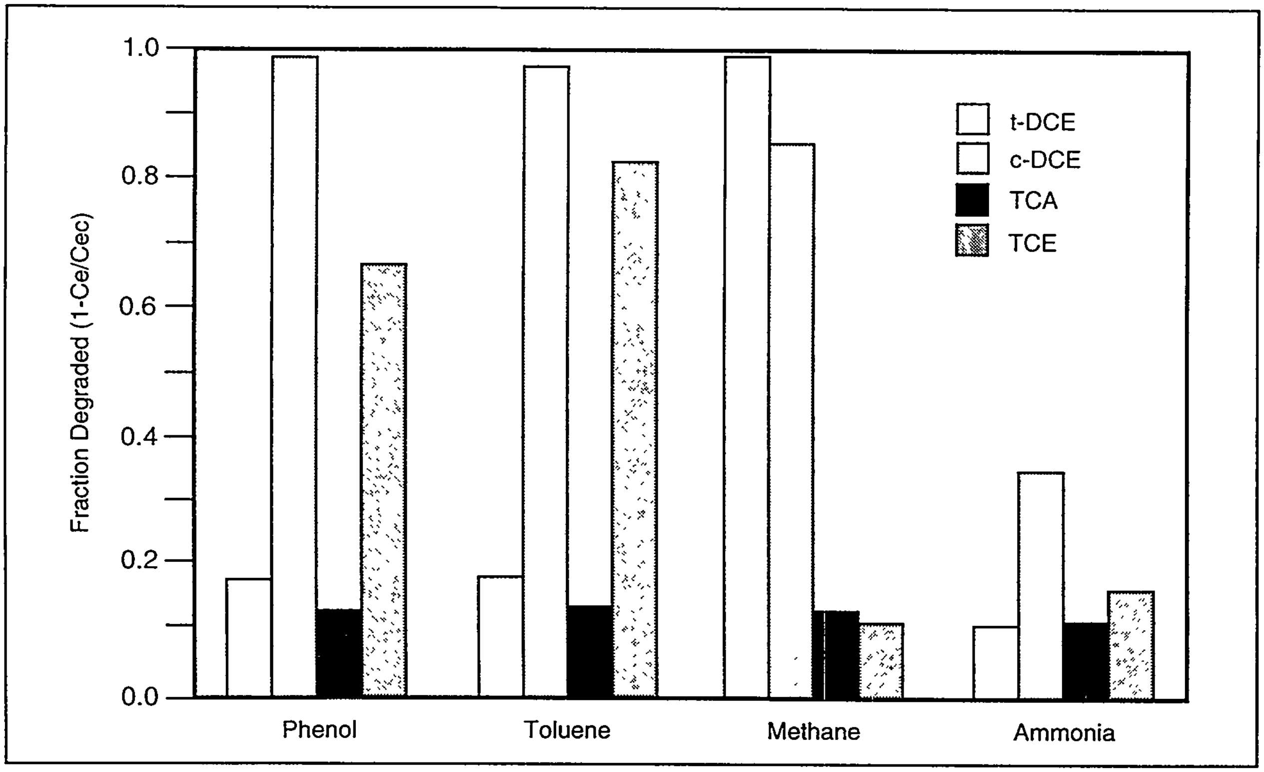

Figure 4.25. Relative fractions of CACs degraded in the groundwater by microcosms following stimulation with different primary growth substrates.

(VC) for introduction into a confined aquifer about 4 m below the surface that is about 1.2 m deep and 6 m long. The growth of the native phenol-degrading population, and the rate and extent to which the introduced chlorinated compounds are removed will be continuously monitored by automatic extraction of groundwater from monitoring wells and on-site analysis. The extent of transformation will be evaluated through comparison of concentration decreases with conservative tracers.

TECHNOLOGY NEEDS

Chlorinated aliphatic compounds are a major contamination of groundwater at many DOE and EPA sites that require remediation.

Bioremediation of groundwaters offers great promise because it results in destruction of contaminants. Application of promising techniques requires research and demonstration at full scale. Field and laboratory studies at Stanford University have helped develop a basic understanding of the processes involved in methanotrophic treatment of chlorinated aliphatic compounds; studies are now in progress with phenol utilizing bacteria and cometabolism with toulene-oxygenase microorganisms. Application of potential technologies is also being evaluated through demonstration in the field.

ACCOMPLISHMENTS

Laboratory-scale bioreactors were used to evaluate the relative performance in chlorinated aliphatic transformations by methane, phenol, toluene, and ammonia-oxidizing bacteria. Toluene and phenol were equivalent in performance, but different from that by methane, and much better by some compounds. Field testing with phenol injection to determine effectiveness with TCE, Cis-DCE, and trans-DCE transformation is now complete with results that are consistent with the laboratory-scale studies. Effective transformation of TCE and Cis-DCE was achieved, but trans-DCE transformation was limited. A report on these results has been prepared.

The studies were especially successful and have led to a great deal of interest in this technology. A number of publications have resulted from this research.

COLLABORATION/TECHNOLOGY TRANSFER

This research is a collaborative effort between the EPA, DOE and Stanford University. Moffett Naval Air Station and the San Francisco Bay Region of the California Water Quality control Board provided logistical support to this study.

A full scale application of the technology developed from this study has been proposed at an Air Force Base in Tucson, Arizona.

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4.26

INDIVIDUAL METAL REMOVAL/RECOVERY BY A NOVEL HOLLOW FIBER MEMBRANE-BASED SYNERGISTIC EXTRACTION TECHNIQUE

TASK DESCRIPTION

The feasibility, efficiency and usefulness of individual metal removal from a mixed waste stream by a novel hollow fiber membrane-based synergistic extraction technique will be investigated (see Figure 4.26). The researcher will employ a module having two separate sets of microporous hollow fibers, one having an acidic organic extractant in the bore and the other having a basic extractant. Metals present as cations will be extracted from the mixed waste flowing in the shell-side of the device into the acidic extractant stream while metals present as anions will be extracted into the basic extractant stream synergistically. For fractionation of individual cations, modules in series with an aqueous raffinate pH control will be used. Base extraction into water will be studied to concentrate and recover individual metals.

The goals of this project will be achieved in a stepwise fashion:

(1) Procure fibers/modules and/or build modules.

(2) Build a flow loop for continuous and simultaneous solvent of cations and anions into different organic extractant streams.

(3) Study extraction equilibrium behavior of each individual metal between aqueous solutions of various concentrations and the organic extractant. Also study mixed metal systems.

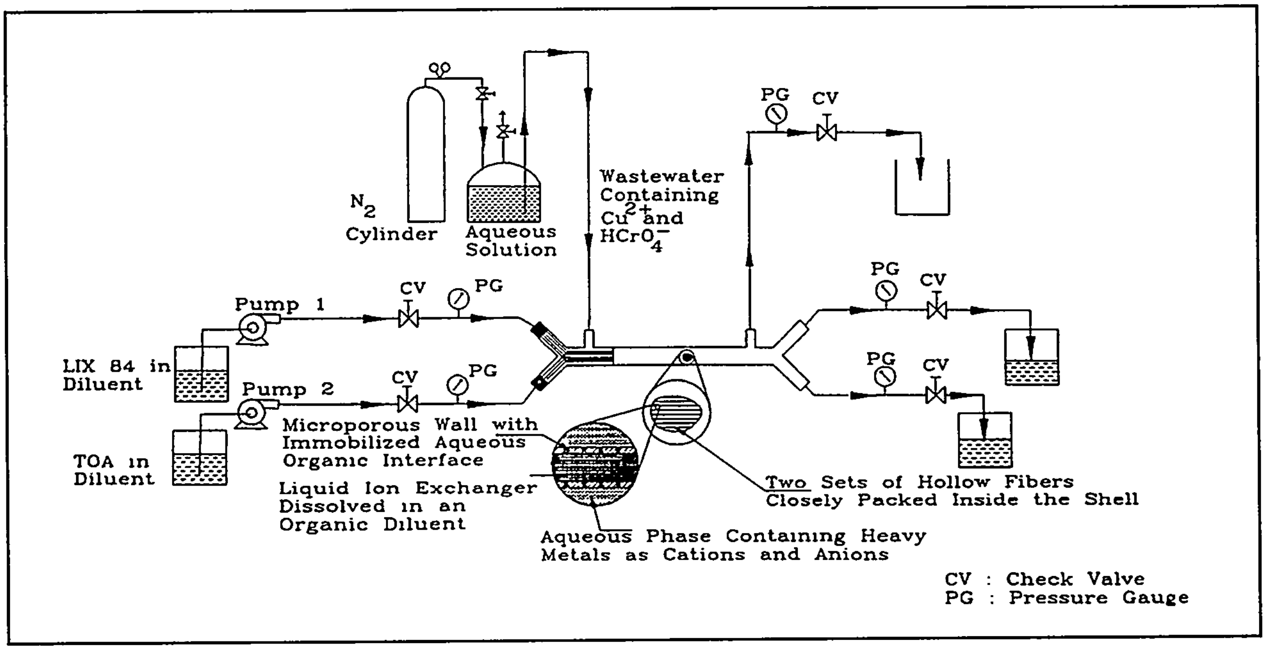

Figure 4.26. Setup of Novel Synergistic Membrane-Based Extractor for the removal of heavy metals from wastewater.

(4) Study simultaneous extraction of Cr^{6+}, Cu^{2+}, Zn^{2+} from an aqueous solution into different organic extractant streams.

(5) Study back extraction of individual metals.

Copper, zinc and chromium levels in aqueous solution will be measured in an Atomic Adsorption Spectrophotometer (Thermal-Jarrel Ash Model 12) located at Hazardous Substance Research Center, New Jersey Institute of Technology (NJIT), Newark, NJ. The pH will be measured by a standard pH meter.

TECHNOLOGY NEEDS

Highly radioactive wastes as well as electroplating shop waste streams contain multiple heavy metals. There is need for developing novel membrane-based synergistic solvent extraction technologies to remove individually the heavy metals and concentrate them for recycling and reuse.

There is a need for innovative separation technologies for individually removing and concentrating a variety of metals found in waste streams from electroplating, nuclear, electronic and chloralkali industries. Currently these metals are removed via precipitation which creates an additional sludge for disposal. If this research is successful, waste minimization along with possible recycling and reuse of the individual heavy metals will result. The research is to demonstrate the feasibility of the concept and will simultaneously provide a basis for technology development.

ACCOMPLISHMENTS

- A module having two separate sets of microporous hollow fibers has been fabricated; through the bore of one set of fibers flows an acidic organic extractant; through the bore of the other set of fibers flows a basic organic extractant.
- Metals present as cations were extracted from the mixed waste flowing in the shell-sides of the device into the acidic extractant stream while metals present as anions were extracted into the basic extractant stream synergistically.
- A model having one set of microporous hollow fibers for fractionation of individual cations has been fabricated.

COLLABORATION/TECHNOLOGY TRANSFER

This research is sponsored by the EPA and DOE and carried out at NJIT.

The emerging technology may be useful to the electroplating, electronic and chloralkali industries for extraction of a variety of metals from their waste streams.

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4.27 INNOVATIVE TREATMENT AND BANK STABILIZATION OF METALS-CONTAMINATED SOILS AND TAILINGS ALONG WHITEWOOD CREEK, SOUTH DAKOTA

TASK DESCRIPTION

Research in this area has been ongoing for the past several years. The research to date has focused on establishing two populations of *Populus spp.* trees.

The proposed remediation technique involves use of a vegative cover that develops deep tree root systems to stabilize mine tailings that have deposited in the Whitewood Creek watershed. Stabilize means to physically decrease particulate movement by developing a biomass cap and decrease the development of leachates that migrate to water supplies by increasing the evapotranspiration of precipitation and seeping groundwater.

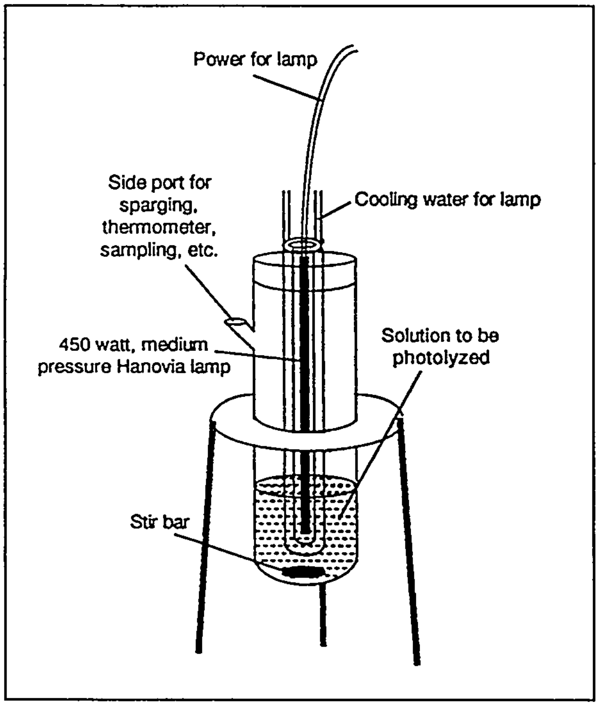

Figure 4.27. Experimental setup for stabilization of metals contaminated soils.

The HMC tailing deposits in the Whitewood Creek creek watershed often have low biomass growth. There appears to be four major stresses on plants:

1. The area is dry. The average rainfall in this region is approximately 50 cm. (20 in.). The 1988 through 1991 growing seasons have been dryer than normal. Many trees require a large moisture reserve to grow.
2. The soil contains many heavy metals which can be phytotoxic at high concentrations. Plants also can take up arsenic, an element with known toxic properties to apple trees.
3. The tailings are low in bioavailable nutrients. The tailing-derived soils have coarse, sand-size particles that do not retain large amounts of water. The nutrient and water availability is fundamental to survival and vitality.
4. The beaver, muskrat, deer, and other grazing wildlife are capable of stressing available trees, especially if there is a shortage of other food sources.

The first poplar population is in a growing chamber located in the Engineering Research Facility. A growing chamber supplied by pH Environmental is being used to control the environmental stresses on poplar cuttings, Imperial Carolina var., planted in groups of three in 12 pots. The experimental design is testing whether the trees can grow in pure tailings or a tailing/soil blend. Phosphorus fertilization impact on growth and survival is also being monitored (see Figure 4.27).

The second poplar population has been planted in the Whitewood Creek watershed on Upper Vale Road near the confluence of Whitewood Creek and the Belle Fourche River. Three sites were planted with poplar trees; in total, approximately 5000 cuttings were planted.

TECHNOLOGY NEEDS

Technology being developed under this project can be useful for stabilizing hazardous waste sites or uranium mill tailings.

ACCOMPLISHMENTS

- Deep-rooted poplar trees have sufficient survival to determine arsenic phytotoxicity and root growth. It will be possible to examine root microryze if such research data is desired.
- Lab scale exploration of the photochemical leachate treatment process has progressed according to schedule. Tailings from the site contain sufficient Fe(III) to generate substantial amounts of soluble Fe(III) oxide, contain ligands which are capable of accelerating the photochemical reduction process.
- Several research papers have been published.

COLLABORATION/TECHNOLOGY TRANSFER

This research project is a collaboration between the EPA, DOE and the University of Iowa.

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4.28 INVESTIGATION ON THE FATE AND BIOTRANSFORMATION OF HEXACHLOROBUTADIENE AND CHLOROBENZENES IN A SEDIMENT-WATER ESTUARINE SYSTEM

TASK DESCRIPTION

The purpose of the proposed research is to investigate the mechanisms and transformations related to the fate of halogenated organic compounds—such as hexachlorobutadiene, hexa-penta-, tri- and dichlorobenzenes—found in the sediments of Bayou d'Inde. The role of the metals, especially iron and manganese, in the fate and transformation of the chlorinated organic compounds will also be investigated.

The objectives of the proposed study are: (a) Physical, chemical and microbiological characterization of selected sites in the contaminated sediment/water estuarine system; (b) Assessment of the rate and extent of biotransformation of the target halogenated organic contaminants; and (c) Investigation of the abiotic release and binding mechanisms responsible for the fate of the target halogenated organic compounds. Two sampling stations in Bayou d'Inde (test sites) and another in the Calcasieu River above the saltwater barrier (control site) will be chosen for water and sediment sampling. Physical, chemical and microbiological analyses will be performed on these samples. Batch biotransformation cultures will be developed for the assessment of the type, rate and extent of biotransformation of the target chlorinated organic contaminants. Abiotic processes (such as volatilization, adsorption/desorption and resuspension) will also be assessed. Rate expressions for all studied processes will be developed.

TECHNOLOGY NEEDS

In spite of major efforts to protect the nation's waterbodies from toxic chemicals, continued problems in aquatic ecosystems persist. Contaminated bottom sediments, previously thought of as "natural sinks" for contaminants in aquatic ecosystems, are now viewed as the source of contamination. Due to the persistence of the sediment contaminants, emphasis has recently been placed on the fate and transport of the in-place pollutants. Although research on contaminated sediments has been intensified in the last decade, we still lack fundamental knowledge of the processes and process interactions that govern the partitioning and transformation of sediment-bound toxic chemicals.

For the purpose of the proposed research project, Bayou d'Inde, a tributary of the Calcasieu River in Southwestern Louisiana, was chosen for study because recent investigations and monitoring of this tributary by state and federal agencies have shown that high-molecular-weight chlorinated organic compounds (benzenes and butadiene) and metals (chromium, copper, lead, mercury, nickel) persist in the sediments. In addition, seafood species were found to be contaminated with hexachlorobenzene and hexachloro- 1 3-butadiene and sediments produced chronic toxicity to aquatic life.

The anticipated results of the proposed study will provide the basis for appropriate decisions as to the remediation options for the contaminated sediments—either in situ or in confined disposal facilities—and for the development of sound regulatory policies and exposure/risk assessments. The contaminants and the processes to be studied are not unique to the Bayou d' Inde tributary but concern other contaminated sediments nation-wide. Therefore, the expected results of the proposed study will have much greater significance and broader applicability.

ACCOMPLISHMENTS

- Water and sediment samples were collected. Parameters and constituents analyzed included pH, alkalinity, major cations, total organic carbon and dissolved organic and inorganic carbon. Several chlorinated organic compounds were extracted from the sediment.
- Desorption experiments were performed in batch reactors. Extremely slow desorption kinetics were observed.
- Biotransformation experiments have targeted the degradation of sediment contaminants under methanogenic conditions simulating in-situ conditions.
- Preliminary results have been presented at a Symposium in April 1993.

COLLABORATION/TECHNOLOGY TRANSFER

This is a collaborative research effort between the EPA, DOE and Georgia Institute of Technology. The technology is still in the exploratory stage. More progress has to be made before this technology can be applied for site remediation.

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4.29

MICROBIAL TRANSPORT IN POROUS MEDIA

TASK DESCRIPTION

The goal of this project is to develop a phenomenological basis for the design and operation of systems for injection/infiltration of microorganisms to enhance contaminant biotransformation in soil and ground water. Improved understanding of microbial transport phenomena is also needed to better predict the subsurface migration of pathogenic bacteria and viruses.

This project will build on research currently being conducted at Kansas State University's HSRC program which has addressed two main objectives: 1) evaluation of transport characteristics of starved and motile cells through porous media, and 2) a study of the ecology of mixed cultures in diatomaceous earth bioreactor packing. This ongoing research has demonstrated the importance of developing a fundamental understanding of porous media microbial transport phenomena to help guide future strategies for bioremediation of contaminated soil and ground water.

This project will investigate the microbial transport processes of advection, dispersion, and adsorption in laboratory core systems under conditions which minimize the effects of cell growth. A variety of media types will be used including glass beads, sand, soil, diatomaceous earth pellets, and field core samples from a benzene tolulene ethylbenzene xylene (BTEX) spill site. Important research questions include: 1) what subsurface environmental conditions affect sticking efficiency and thus determine the dimensions of the zone of penetration of injected/infiltrated cells? 2) can the zone of penetration be manipulated by varying injection flow rate, inoculum concentration or other control variables?

The project objectives are as follows: 1) Determine the effects of flow rate and influent suspended cell concentration, along with porous media properties (i.e., porosity, permeability, and organic carbon content) on advection and adsorption of pulse injections of microbial inocula through saturated porous media cores and diatomaceous earth pellets. 2) Construct and test apparatus for monitoring microbial transport and accumulation through variably-saturated cores. 3) Determine the effects of variable soil moisture content on transport and accumulation of microbial inocula infiltrated through vertical core systems. 4) Determine the accuracy with which microbial transport phenomena (i.e. advection, dispersion, and adsorption) can be predicted using BIOSIM, an existing microbial process simulation model). Data obtained from Objectives 1-3 will be used to calibrate and verify the model.

TECHNOLOGY NEEDS

Schemes for enhancing *in situ* bioremediation of contaminated soil and ground water generally involve injection and/or infiltration of fluid, nutrients, and oxygen (or other electron acceptor) to stimulate growth of native microbial populations in the subsurface. In addition, suspended cultures of contaminant degrading organisms may be added to the process stream to increase the amount of attached and suspended biomass within subsurface porous media as well as in packed bed pump/treat systems. Presently, little is known concerning transport, accumulation, and fate of injected microorganisms and consequently, the rational design and operation of microbial injection/infiltration systems is difficult.

Priority research in this region focuses on cleanup of soil and water contaminated by a variety of organic chemicals. This research project will develop improved strategies for using microbial injection to enhance *in situ* bioremediation and is therefore relevant to research needs within the region pair. In addition, the fundamental understanding of microbial transport phenomena will improve prediction of subsurface migration of pathogens released from septic tank leach fields and other sources.

ACCOMPLISHMENTS

- A fully operational core test system for measuring microbial transport under variably saturated flow conditions has been established.
- An assessment of the accuracy with which microbial transport variables can be predicted using the BIOSIM model has been completed.
- Two papers have been published.

COLLABORATION/TECHNOLOGY TRANSFER

The Engineering Research Center (ERC) at Montana State University and CONOCO'S Environmental Research Division will be industrial collaborators. The project will be conducted in the ERC laboratories using a recently-developed porous media core testing system. Funding is provided by the EPA and DOE.

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4.30 MODELLING OF THE USE OF PLANTS IN THE REMEDIATION OF SOIL AND GROUNDWATER CONTAMINATED BY HAZARDOUS ORGANIC SUBSTANCES

TASK DESCRIPTION

The objectives of this project are to: (1) develop and verify models to simulate the fate of hazardous organic substances in a transpiring plant's root zone; and (2) use the simulation models to engineer plant remediation strategies for contaminated ground water and soil sites.

The initial step in this study is to perform an exhaustive review of the available literature related to the fate of hazardous organic substances in a plant's root zone. Models are currently being formulated to simulate the fate of organic substances in a plant's root zone by first developing and then combining the three significant model components, which are: (1) the fate of the contaminant in the rhizosphere; (2) the transport and uptake of the contaminant by the root system; and (3) the fate of the contaminant in the plant. Once the models are fully developed and verified, they will be used to engineer a plant remediation strategy for a site contaminated with hazardous organic substances.

TECHNOLOGY NEEDS

Much of the population in EPA Regions' 7 and 8 rely on ground water for their potable water supply. Recent studies have shown that many ground water aquifers within this region have been contaminated with hazardous organic chemicals that are by-products of agricultural production or have leaked from disposal sites. Due to the large scale nature of the soil contamination involved in these types of problems, conventional soil and ground water remediation techniques would prove to be very expensive or impractical. Recent studies have demonstrated the potential for plants to play an important role in remediating soil and ground water contaminated with organic substances. However, before this new technology can be put into use, a method will have to be developed to predict the effects that plants have on soil and ground water remediation, so that effective planting and management plans can be developed.

ACCOMPLISHMENTS

- Completed review of the available literature and current research into the fate of hazardous organic contaminants in a root-soil environment.
- Work has begun on preliminary laboratory experiments and the development of the biochemical degradation, contaminant transport and uptake models.
- Completed the theoretical framework for models describing the biochemical degradation, transport and uptake of hazardous organic chemicals in a root-soil environment.
- Analyses using the models are now being performed to determine the significant processes involved in determining a contaminant's fate in a root-soil environment. The results of these analyses will help define the level of complexity necessary to accurately describe the fate of a contaminant in a root-soil environment.

- The model describing the transport and uptake of contaminants by a transpiring plants' root system was recently presented at the 1991 Hazardous Waste Conference at Kansas State University.
- The biodegradation model will be presented at the upcoming AIChE meeting.
- Preliminary laboratory experiments were constructed to determine the tolerance of various deep rooted plant species to organic solvents.
- Preliminary tests using Cottonwood trees and alfalfa as the main test subjects have thus far shown that saturating levels of toluene in an aqueous solution can be tolerated by these plants in a perlite vermiculite medium.
- Selected a site for engineering a plant remediation strategy.

COLLABORATION/TECHNOLOGY TRANSFER

Collaborating in this research project are the EPA, DOE, South Dakota State University and the University of Iowa.

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4.31 NANOSCALE METAL OXIDE PARTICLES AS REAGENTS FOR DESTRUCTION AND IMMOBILIZATION OF HAZARDOUS SUBSTANCES

TASK DESCRIPTION

The intent of this project is to synthesize new, ultrafine metal oxide powders, characterize these materials, and test/develop them as destructive adsorbents for toxic substances, especially chloroorganic compounds. This new technology is based on ultrahigh surface area metal oxides with reactive surfaces that behave as "destructive adsorbents." Research objectives are : 1) to develop the best way of synthesizing the destructive adsorbents, 2) to understand the surface chemistry going on during the adsorption/destruction process, and 3) to develop a second generation of better destructive adsorbents based on multilayer oxide/oxide composites. These reagents, for example, activated metal oxides, will be chosen on the basis of their widespread and inexpensive availability, their rapid dealkylative, hydrolytic, and/or oxidative decompositions of the target chemical, and their extensive reaction capacity. For the best results, volatile non-polar products such as hydrocarbons and ethers, would form and be desorbed, while polar components containing the heteroatom would bind strongly to the metal oxide. After decomposing large amounts of reagents, the oxides would eventually lose activity and be discarded.

TECHNOLOGY NEEDS

Destructive adsorbent technology has promise as an alternative to incineration, and for air purification systems. This technology is applicable to many toxins, including phosphorus, nitrogen, sulfur, and halogen containing compounds. In the present context chlorocarbons are of most interest.

ACCOMPLISHMENTS

- Results indicate that for metal oxides to be effective destructive adsorbents for chlorocarbons, three parameters are critical: (1) high surface area; (2) surface basicity; and (3) favorable thermodynamics.
- Ultrahigh surface area Fe_2O_3 on MgO surpasses all the numerous other that were tested.
- The high capacity of Fe_2O_3/MgO for CCl_4 destructive adsorption of CCl_4 is apparently due to a "spillover" catalytic effect as yet unknown in the literature.
- It appears that Cl/O exchange takes place on Fe_2O_3, and then Cl spillover onto MgO where another Cl/O exchange takes place. In this way, much more MgO is converted to $MgCl_2$.
- Several presentations and publications have resulted from this project.

COLLABORATION/TECHNOLOGY TRANSFER

Collaborators in this research project are the EPA, DOE and the Kansas State University.

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4.32 PHASE EQUILIBRIA AND TRANSPORT PROPERTIES OF SURFACTANT SYSTEMS OF INTEREST TO SOIL REMEDIATION

TASK DESCRIPTION

The goal of this project is the design and evaluation of surfactant-enhanced aquifer remediation (SEAR) technologies for the cleanup of aquifers contaminated with nonaqueous phase liquids (NAPLs). The process consists of injecting surfactant solutions into NAPL-contaminated aquifers. Immediate objectives of the project are limited to (1) investigate phase equilibria in surfactant/organic/water systems of interest to aquifer remediation; (2) develop efficient and environmentally acceptable surfactant formulations for SEAR (see Figure 4.32); (3) determine the extent to which phase behavior can be utilized to design and evaluate SEAR processes. Two NAPL removal processes were considered: (1) solubilization by an aqueous micellar solution, and (2) mobilization by middle phase microemulsions. The project was divided into the following tasks: (A) surfactant selection and screening, (B) formulation of middle phase microemulsions for SEAR, (C) experimental investigations for hydrocarbon solubilization in micellar solutions of biodegradable and non-toxic ethoxylated non-ionic surfactants, and (D) development of semi-empirical correlations to estimate solubilization capacity as a function of surfactant and hydrocarbon molecular properties.

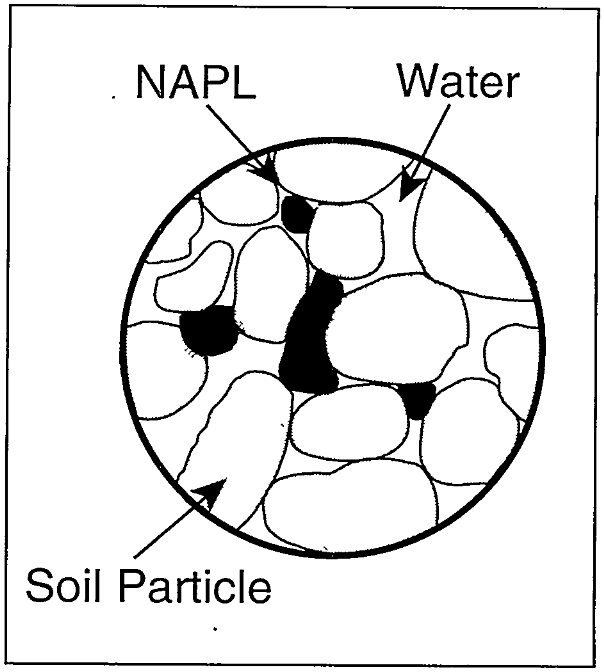

Figure 4.32. Surfactant-enhanced aquifer remediation (SEAR).

TECHNOLOGY NEEDS

Polycyclic aromatic hydrocarbons, pesticides and other water-insoluble carbon compounds (NAPLs) are among the hazardous chemicals found in contaminated soil at several DOE sites. Remediation is generally by excavation of contaminated soil and its disposal in RCRA Subtitle C permitted landfills, or incineration. The former is uneconomical and the latter has fallen into dispute. Promising among the alternative technologies examined is surfactant-enhanced remediation of aquifers and soils. Success depends upon identification or development of the right surfactant and establishing conditions for optimal performance. Given the proper input, this technology has the potential for successful implementation.

ACCOMPLISHMENTS

- Three nonionic surfactants were selected for study. The solubilization capacity of these surfactants for two model hydrocarbons, dodecane and perchloroethylene were found to increase by approximately six orders of magnitude and 400-fold respectfully, in aqueous surfactant solutions.

- Explored formulations of cosolvent/salt-free middle phase microemulsions for mobilizations based SEAR processes. Results of exploratory research indicated the need to synthesize surfactants with no cosolvency requirements.
- Results were presented at the American Chemical Society (ACS) symposium and published in Environmental Science and Technology, September, 1993.

COLLABORATION/TECHNOLOGY TRANSFER

Collaborators in this research project are EPA, DOE, State of Michigan Department of Natural Resources and the University of Michigan.

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4.33 RADON-222 METHOD FOR LOCATING AND QUANTIFYING CONTAMINATION BY RESIDUAL NON-AQUEOUS-PHASE LIQUIDS IN THE SUBSURFACE

TASK DESCRIPTION

The objectives of this research are to develop and demonstrate the proposed geochemical method for detecting and quantifying residual NAPL contamination in the saturated zone. Specific objectives are:

1) to determine needed model parameters including radon partition coefficients between aqueous and pure NAPL phases and radon emanation coefficients from model aquifer solids into the aqueous and pure NAPL phases;

2) to evaluate the method under controlled conditions in the laboratory;

3) to evaluate the method in the field in a controlled experimental setting where NAPLs are in the saturated zone;

4) to apply the method in a controlled field experiment, where remediation of NAPLs is being performed to assess the progress of remediation.

TECHNOLOGY NEEDS

Subsurface contamination by organic compounds present as NAPLs is being encountered with greater frequency as sites are studied in more detail. NAPLs can be a long-term source of groundwater contamination, as they slowly dissolve. The presence of undetected NAPLs may be one of the factors contributing to the long times required for pump-and-treat remediation at some sites as the NAPLs act as a source of dissolved contaminants. In their review of NAPL contamination in the subsurface, Mercer and Cohen stressed the need for methods to detect and quantify NAPL contamination in the subsurface. This research will focus on the development of a geochemical method for detecting and potentially quantifying NAPL contamination in the subsurface.

The method relies on measurements of naturally occurring radon-222 concentrations in subsurface fluids. The method will focus on detecting residual NAPL contamination (immobile) in the saturated zone, based on aqueous-phase radon concentrations in groundwater samples from monitoring wells. As will be demonstrated, radon's unique properties should result in a distinct concentration signal in groundwater samples when immobile NAPL is present in or near the zone from which the samples are obtained. This research will develop the radon geochemical method for detecting and quantifying NAPL contamination using a combination of laboratory and field studies.

ACCOMPLISHMENTS

- Laboratory studies have been conducted on aquifer solids and radon partitioning into NAPLs has been determined.

- Field studies confirmed that radon deficits occur in the presence of residual NAPL contamination.

- Demonstrated that radon deficits occur locally in the NAPL source zone, but rapidly reequilibrate to background conditions upon leaving the source zone.

- Studies indicate that the radon method is sensitive to change in NAPL saturation over short spacial scales and might be used to characterize NAPL source areas.

- The radon method might also be used to monitor the process of NAPL remediation.

- Poster presentation at Oregon State University in August 1993.

COLLABORATION/TECHNOLOGY TRANSFER

The project is being conducted in collaboration with the Waterloo Center for Groundwater Research, Waterloo, Ontario, Canada and Borden is being used as the test site.

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4.34 REDUCTIVE DECHLORINATION OF CHLORINATED AROMATICS BY BACTERIAL TRANSITION METAL ENZYMES

TASK DESCRIPTION

The purpose of this research is to examine the reductive dechlorination of chlorinated aromatic compounds such as polychlorinated biphenyls (PCBs) and chlorinated benzenes. Dechlorination reactions are mediated by vitamin B_{12} in controlled cell-free biomimetric systems. These reactions are studied in order to gain insight into the reductive dechlorination process.

The specific objectives are to determine the relative redox potentials of various PCBs cogeners and chlorinated benzenes and the influence of chlorine substitution patterns on the relative rates of aromatic reductive dechlorination. The experimental system consists of a chemical reducing agent and electron donor to maintain a constant low redox potential (e.g. titanium citrate), an electron transfer mediator (e.g., vitamin B_{12}), and the chlorinated aromatic compound. The medium is pH buffered (Tris) and contains a water miscible solvent (tetrahydrofuran) to provide constant and relatively high initial concentrations of the different hydrophobic chlorinated aromatic compounds to be studied. Gas chromatography, with an electron capture detector, is used to measure concentrations of initial compounds and monitor appearance of products.

TECHNOLOGY NEEDS

Remediation of chlorinated aromatics contaminated soils and water is accorded high priority in environmental restoration activities at DOE sites. In nature, the major degradative pathway for heavily chlorinated aromatics is through reductive dechlorination. Currently, the environmental, chemical, and microbial conditions required for the microbially-mediated reductive dechlorination of aromatic compounds are not well understood. More information on the reductive dechlorination process is needed without which engineering an improved process could not be put into effect for degradation of this class of pollutants. It is hoped that the current project will provide insight into understanding this complex process. Knowledge of conditions necessary for reductive dechlorination will also improve assessment of in-situ bioremediation projects.

ACCOMPLISHMENTS

- Experimental conditions and analytical methods were optimized. The effective pH range of Tris buffer was 7.5-9.5. The dechlorination rate of hexachlorobenzene increased with increased pH.
- Demonstrated that vitamin B_{12} can mediate reductive dechlorination at a stoichiometric ratio of less than 1:1.
- The mediator is recycled in the experimental system and is not transferred or deactivated.
- Two papers are proposed to be published.

COLLABORATION/TECHNOLOGY TRANSFER

This is a collaborative research project between EPA, DOE and the University of Michigan. Results have the potential of being used in the decontamination of hydraulic and electrical equipment containing PCB and chlorinated benzenes.

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4.35 REMEDIATION OF CONTAMINATED AQUIFERS WITH SURFACTANTS: EFFECT OF SURFACTANT SORPTION AND DESORPTION

TASK DESCRIPTION

Surfactants are being actively investigated as promising agents for remediation of contaminated aquifers. The goal of this project is to ultimately come up with guidance for application to actual groundwater remediation schemes.

The major objective is to carry out a detailed study of surfactant sorption/desorption on clays, mineral oxides, and naturally occurring soils and porous media. Two solids (quartz and hectorite), two surfactants (CAB and CPC), and two PAH compounds, naphthalene and pyrene, will be studied (see Figure 4.35).

TECHNOLOGY NEEDS

Containment and cleanup of groundwater contaminated by polycyclic aromatic hydrocarbons (PAHs) is of growing concern at several DOE sites. Bioremediation is considered one of the most attractive decontamination processes for PAHs. Because insitu biodegradation of PAHs is very slow, additional action is often needed to keep a contaminant plume from migrating to nearby water supplies before complete biodegradation has occurred. Cationic surfactants hold the potential to substantially increase the soils sorption capacity for contaminants and reduce their mobility, allowing sufficient time for biotransformation to take place. This research examines that feasibility.

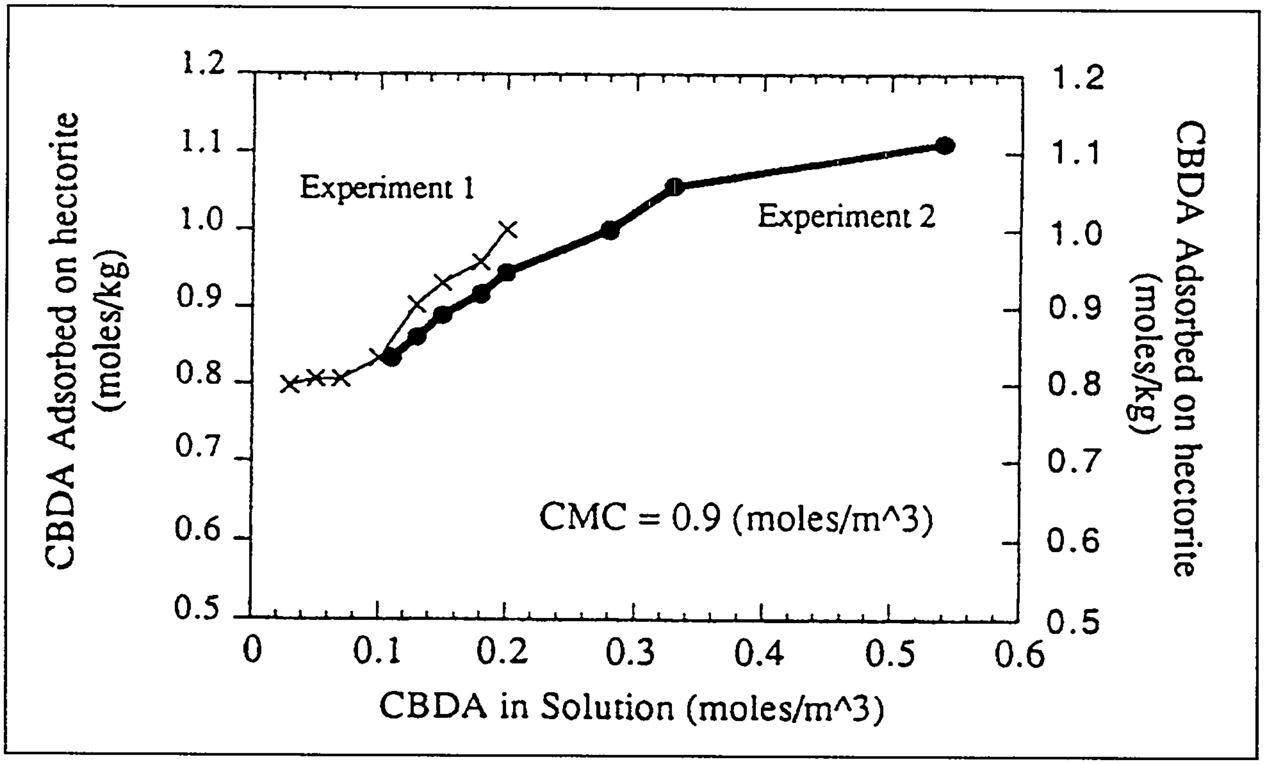

Figure 4.35. Sequential desorption of CBDA from CBDA-hectorite.

ACCOMPLISHMENTS

- Using cetylbenzyl dimethylammonium (CBDA) as the cationic surfactant and phenanthrene as the target pollutant, it was demonstrated that CBDA is irreversibly adsorbed onto smectite at sub-equivalent coverage and phenanthrene partitioning is substantial even at low surface coverage.

- Confirmed that the amount of CBDA irreversibly sorbed is in the interlayer region.

- The results imply that PAHs, such as phenanthrene, can be most effectively immobilized at low surfactant coverage.

- Investigators made several presentations and published papers.

COLLABORATION / TECHNOLOGY TRANSFER

EPA, DOE and University of Michigan collaborated in this research project.

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4.36 REMOVAL OF CONTAMINANTS FROM THE VADOSE ZONE BY PNEUMATIC FRACTURING

TASK DESCRIPTION

Pneumatic fracturing is an in-situ process which enhances the removal and treatment of hazardous organic contaminants from the vadose zone. The process consists of injecting high pressure air or other gas into contaminated geologic formations at controlled flow rates and pressure (see Figure 4.36).

. The objectives of this research project are to:

1) develop and validate with field data an analytical model for prediction of pneumatic fracture initiation pressure;

2) conduct theoretical studies including thermodynamic effects of pneumatic injection and formulation of a dual porosity model for VOC transport through a fractured formation;

3) apply a vapor extraction system to the soil apparatus and compare the contaminant removal rates between fractured and unfractured soils;

4) conduct field demonstrations at several contaminated sites; and

5) integrate pneumatic fracturing with bioremediation.

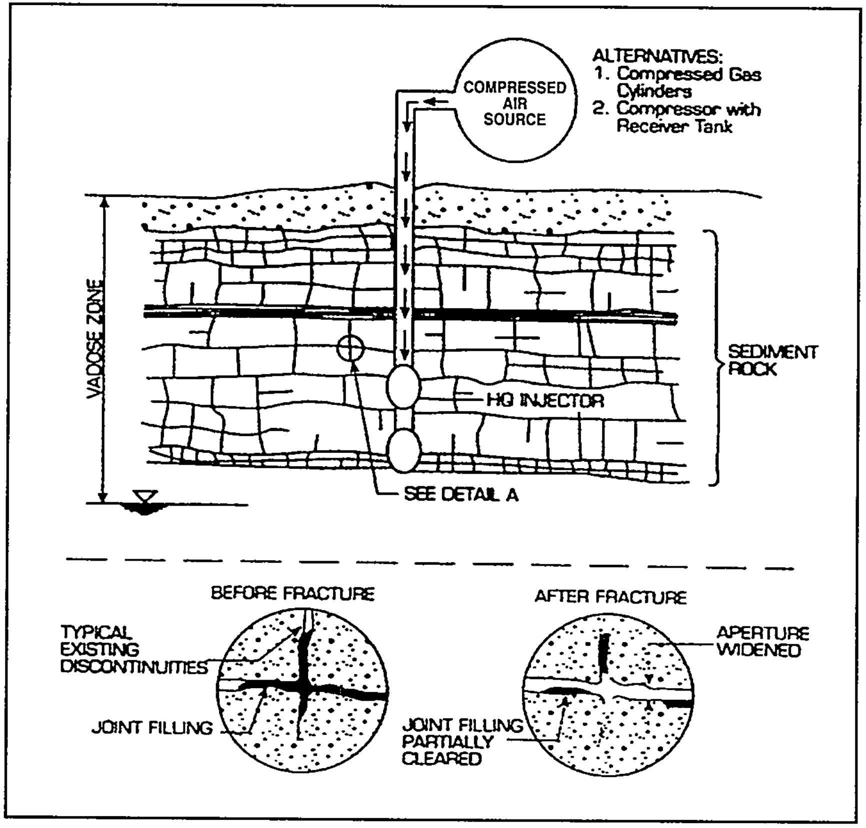

Figure 4.36. Effect of fracturing on rock discontinuities.

TECHNOLOGY NEEDS

Of the emerging technologies for removal and treatment of hazardous organic contaminants from the vadose zone, pneumatic fracturing appears to be a promising one. The technology has potential to reduce treatment time and use in more difficult geologic conditions. Work done hitherto has demonstrated that pneumatic fracturing is a viable technology for in-situ remediation of the vadose zone. The potential benefits of this technology depend on the type of soil or rock being treated. Pneumatic fracturing can be integrated with a number of other in-situ technologies including vapor extraction, bioremediation and thermal treatment. Potential benefits of the technology are significant and deserve to be explored further.

ACCOMPLISHMENTS

- A full-scale prototype system was constructed and field tested at two "clean" sites and two sites containing VOCs.
- Field demonstrations have been conducted at several sites.
- Feasibility of pneumatic fracturing to enhance remediation of the vadose zone was confirmed.
- Field studies demonstrated that fractures remain viable for extended periods.

COLLABORATION/TECHNOLOGY TRANSFER

This research is a collaborative venture between DOE, New Jersey Institute of Technology, Accutech Remedial Systems, Inc., Science Applications International Corporation and McLaren Hart Environmental Engineering.

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4.37

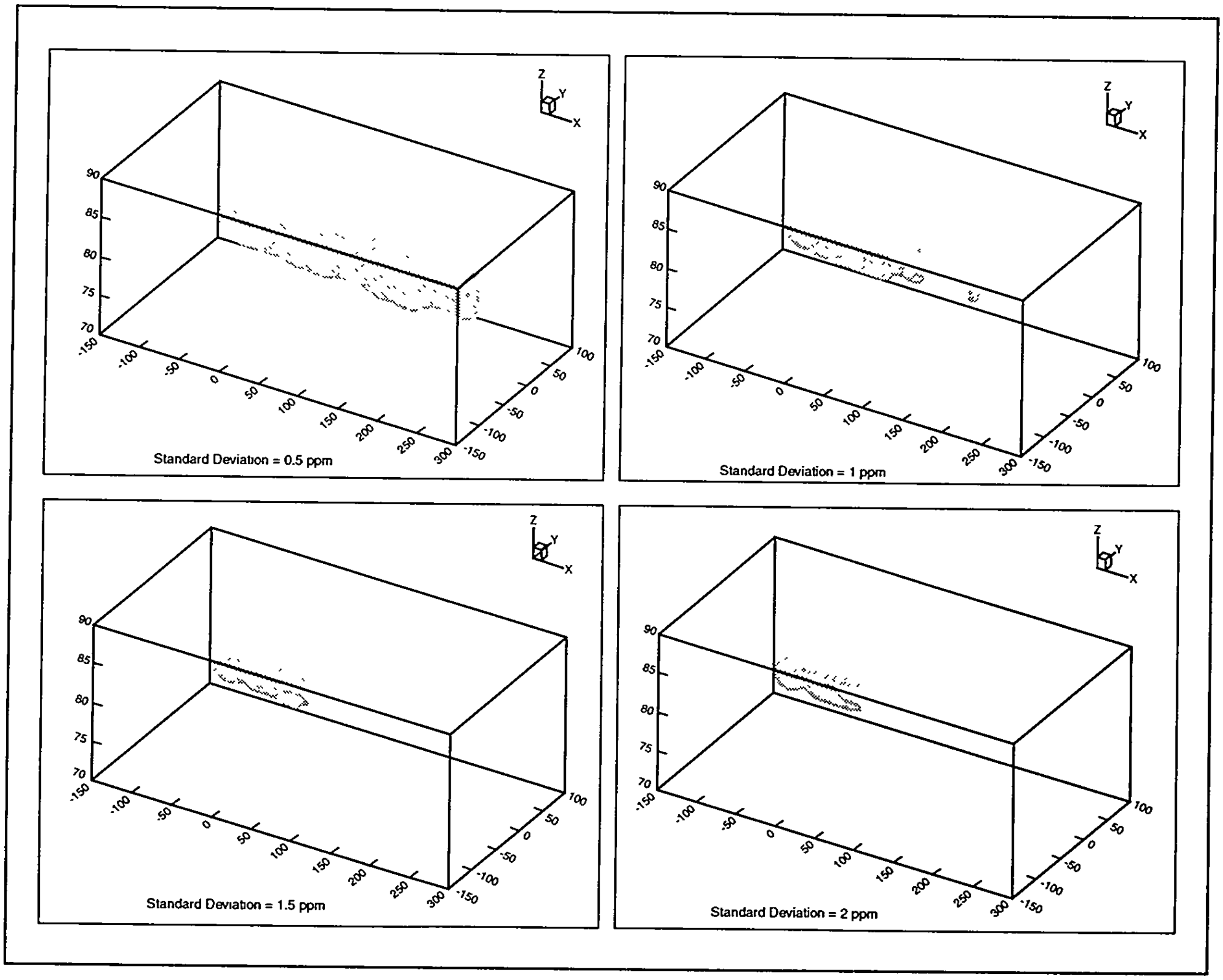
THREE-DIMENSIONAL CHARACTERIZATION OF SUBSURFACE CONTAMINATION BEFORE AND DURING REMEDIATION

TASK DESCRIPTION

The objective of the proposed project is to improve and demonstrate the site characterization procedure that was developed in previous Northeast HSRC projects. This procedure generates three-dimensional maps of subsurface groundwater contamination by combining information from field measurements and physically based computer models. It is based on Bayesian estimation concepts which are similar to those used to produce computer assisted tomography (CAT) scans.

Specific research tasks for the proposed project are summarized below:

1. Extend the existing site characterization procedure so that it can provide maps of soil contamination as well as groundwater contamination.



Standard Deviation = 0.5 ppm

Standard Deviation = 1 ppm

Standard Deviation = 1.5 ppm

Standard Deviation = 2 ppm

Figure 4.37. Naphthalene groundwater concentration uncertainty (standard deviation) associated with a model-based inverse procedure.

2. Extend the site characterization procedure to provide for spatial variability in sorption properties.

3. Test the extended site characterization procedure.

TECHNOLOGY NEEDS

Subsurface contaminant plumes found at hazardous waste sites can be highly irregular and difficult to locate. Large sums of money and time are spent for characterizing such sites. New methods are an urgent need for mapping subsurface soil and groundwater plumes to help assess the severity of contamination problems and to plan remedial programs. Such methods are being developed at the Massachusetts Institute of Technology (MIT) Department of Civil and Environmental Engineering. These techniques are typically developed and tested under controlled laboratory conditions. Although controlled testing is an important part of any research program, the practical value of a new remedial technique is ultimately established in larger field-scale tests. The subsurface environment at a hazardous waste site is much more complex and heterogeneous. As a result, real-world contaminant plumes may not always respond as expected. There is a need to monitor such plumes throughout the remediation process. The proposed project is expected to fill the need for that new technology.

ACCOMPLISHMENTS

- New estimation algorithms which are able to handle the extra computational demands posed by a multi-variable characterization were developed.
- Preremedial soil data and post-remedial groundwater data were assembled and analyzed at a test site in upstate New York.

COLLABORATION/TECHNOLOGY TRANSFER

EPA, DOE and Massachusetts Institute of Technology have collaborated in conducting this research. On completion of the project, site characterization procedure will be available for application to other hazardous waste sites where similar problems are encountered.

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Robotics

Section 5.0

5.0 ROBOTICS TECHNOLOGY DEVELOPMENT PROGRAM OVERVIEW

The Robotics Technology Development Program (RTDP) is a "needs-driven" effort. A lengthy series of presentations and discussions at DOE sites considered critical to the Department's Environmental Restoration and Waste Management (ER&WM) emphasis resulted in a clear understanding of needed robotics applications toward resolving definitive problems at the sites. A detailed analysis of the resulting robotics needs assessment revealed several common threads running through the sites: Tank Waste Retrieval (TWR), Contaminant Analysis Automation (CAA), Mixed Waste Operations (MWO), and Decontamination & Dismantlement (D&D). The RTDP Group realized that much of the technology development was common (Cross Cutting-CC) to each of these robotics application areas, for example, computer control and sensor interface protocols. Further, the OTD approach to the Research, Development, Demonstration, Testing, and Evaluation (RDDT&E) process urged an additional organizational break-out between short-term (1-3 years) and long-term (3-5 years) efforts (Advanced Technology-AT). The RDTP is thus organized around these application areas - TWR, CAA, MWO, D&D and CC&AT - with the first four developing short-term applied robotics. An RTDP Five-Year Plan was developed for organizing the Program to meet the needs in these application areas.

Each application area is coordinated by a DOE contractor at a site/laboratory chosen for its unique expertise or its situation as paradigmatic of an ER&WM problem. The coordinator leads a team of experts chosen from throughout the DOE complex, private industry and universities: an integrated, multi-member, team approach.

The DOE Headquarters Robotics Program Manager, a DOE employee, is responsible for higher level management of the entire Program through consultations throughout ER&WM and frequent interactions with coordinators. Overall program direction, as reflected in fiscal emphasis, is a primary responsibility. Another is program integration between the several RTDP application areas, between the various OTD activities supported by the RTDP and between non-OTD offices in ER&WM. Program integration is critical for resource maximization in meeting needs. The Robotics Program Manager's function can summarily be stated as directly managing the RTDP so as to develop and demonstrate efficacious robotics systems, defined as needed by the supported programs, through a complex-wide integrated approach.

The technology development and program management approach followed by the RTDP can be expressed as:

1) TEAMS - pull together the best from DOE National Laboratories, industries and universities.

2) BROAD APPLICABILITY - focused projects to solve complex-wide problems.

3) NEEDS-DRIVEN - direct contact with sites and supported programs to build required systems.

4) EXTERNAL INTEGRATION - each part of the RTDP is directly mapped onto DOE Headquarters organization.

5) INTERNAL INTEGRATION- emphasis on solutions to common problems within the RTDP for application to supported programs.

6) NATIONAL PERSPECTIVE - address complex-wide solutions through direct management by DOE Headquarters.

A brief description of each Technical Application Area appears below. For a more detailed description of the activities occurring in each of the Technical Application Areas, see the *Robotics Technology Development Program Technology Summary*, February 1994, DOE/EM-0127P.

Tank Waste Retrieval (TWR):

The Tank Waste Retrieval (TWR) Team provides a cost-effective robotics technology base for retrieval of waste from underground storage tanks. Led by PNL, with contributions from ORNL and SNL, this three-laboratory Team works closely with industry and universities to meet program objectives.

The TWR Team provides enhanced research and development tools centered around a robotics test bed and a comprehensive computer-based simulation network shared among the three contributing laboratories. Retrieval-focused robotics technologies are developed by the Team and integrated as part of the test bed demonstration. The Team directly responds to technology needs identified by waste tank remediators and provides robotics technology inputs for tank remediation planning and procurements.

Contaminant Analysis Automation (CAA):

LANL is the lead laboratory in the CAA coordination area. The other laboratories involved in the CAA effort include PNL, INEL, SNL, and ORNL. The CAA thrust is to address the development of technologies necessary for the automation of DOE and DOE-contract environmental laboratories. The CAA Team develops fully automated modules which perform a generic task common to analytical chemistry. The modules are chosen for their repeated use in DOE analysis methods and represent a significant fraction of sample load. The underlying theme is "plug-and-play", interface standardization, transportability, architectural openness and modularity. This effort is in response to the tremendous need for chemical characterization of soil samples; contents of storage tanks, and water samples that must take place before remediation can be initiated.

Mixed Waste Operations (MWO):

The MWO Team is composed of six DOE laboratories and sites working with industry and universities to develop state-of-the-art technology to store and treat low-level and transuranic mixed wastes. The Team, led by the Savannah River Technology Center (SRTC), works closely with the Mixed Waste Integrated Program in identifying and prioritizing needs and opportunities to cleanup over 24,000 cubic meters of low-level mixed waste at DOE sites. In addition to SRTC, participants of the MWO Team include Fernald Environmental Management Site (FEMP), INEL, LLNL, ORNL, and SNL. The Team develops systems for front-end handling and pre-processing of mixed waste containers and contents, plus handling of the final waste forms after processing. Automated inspection of stored waste containers is also a major aspect of the MWO group. Graphical modeling and automation of operations with graphics viewing is a key approach to facilitating operations programming.

Decontamination and Dismantlement (D&D):

There are a large number of contaminated facilities including hot cells, canyons, glove boxes, and reactor facilities, at DOE sites that must eventually undergo some form of decontamination and dismantlement (D&D). As facilities transition from operational use, facility deactivation, followed by a period of surveillance and maintenance (S&M) pose many of the problems that will need to be addressed in ultimate D&D activities. Deactivation and S&M activities place emphasis on characterization, data capture, and selective D&D in order to define and minimize the risk and cost associated with possible long-term S&M activities required prior to final D&D. The overall emphasis of the D&D application area is the automation of the D&D process, from surveillance to facility characterization to surface decontamination to hot cell dismantlement to maximize efficiency while minimizing human exposure. The work centers around vehicular and crane deployed dual-arm systems using advanced sensors, control and operator interface technologies.

Cross Cutting & Advanced Technology (CC&AT):

Several program elements within RTDP have some degree of common technology needs. These common needs, plus the increasing need for technologies that can be directly applied to faster, safer, and more cost-effective robotics systems, are the main focus of the CC&AT Team. The CC&AT Team, coordinated by SNL, with participation by PNL, LANL, and ORNL, develops technologies used throughout the RTDP. Projects are directed toward a generic, graphics robot controller based on an integrated multisensory system plus systems analysis and modeling/simulation. Coupling of sensor-based modeling with automated programming of robot operations is a key approach to developing faster, safer, and less expensive waste clean-up systems.

FY94 Activities Funded Through the Chicago Operations Office

Section 6.0

OFFICE OF TECHNOLOGY DEVELOPMENT EM-50
FY 1994 ACTIVITIES FUNDED THROUGH THE CHICAGO OPERATIONS OFFICE

(By Program Element)

TTP NUMBER	TITLE
VOCs IN NON-ARID SOILS ID	
CH221107	INTEGRATED PULSED ULTRAVIOLET IRRADIATION/DRY SCRUBBING
VOCs IN ARID SOILS ID	
CH221104	DESTRUCTIVE/CONVERSION OF HAZARDOUS WASTE CHLOROCARBONS
CH241005	ARID TECHNICAL SUPPORT
CH241006	IN WELL SONIFICATION
CH341002	ARID TECHNICAL SUPPORT
MIXED WASTE LANDFILL ID	
CH221102	OPTIMIZATION OF SAMPLING STRATEGIES
CH321101	IN SITU CONTAINMENT AND STABILIZATION OF BURIED WASTE
URANIUM IN SOILS ID	
CH221106	AQUEOUS BIOPHASIC TREATMENT OF URANIUM CONTAMINATED SOIL
CH231003	AEM EXAMINATION OF FERNALD SOILS
CH341001	CITRATE BIODEGRADATION
CHARACTERIZATION, MONITORING & SENSOR TECHNOLOGY IP	
CH101103	IMPROVEMENTS IN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY
CH111203	INTEGRATED PROGRAM - CHARACTERIZATION AND SENSOR TECHNOLOGY
CH131001	INFRARED ANALYSIS OF WASTES (FTIR-PAS & TIRS)
CH131002	ZERO TENSION LYSIMETERS
CH131003	AMES MOBILE LABORATORY PROJECT
CH131004	SENSING OF HEAD SPACE GASES & CONTINUOUS IN SITU MONITORING
CH131005	AMES INTEGRATION OF INNOVATIVE EXPEDITED SITE CHARACTERIZATION TECHNOLOGY
CH141001	LA-ICP-AES/HIGH RESOLUTION FIBER OPTIC INTERFEROME
CH141002	ACOUSTIC CHARACTERIZATION-WASTES IN STABILIZED UNDERGROUND TANKS
CH221202	DEVELOP CONTINUOUS EMISSION MONITOR FOR INCINERATORS
CH231001	TECHNOLOGY PERFORMANCE SPECIFICATIONS
CH231004	NEW INITIATIVE ON EXPEDITED SITE CHARACTERIZATION
CH231006	CONE PENETROMETER OPERATIONS
CH241001	IN SITU MEASUREMENT OF VOLATILE & SEMI-VOLATILE ORGANIC COMPOUNDS
IN-SITU REMEDIATION TECHNOLOGY DEVELOPMENT IP	
CH211101	MOUND-BRADTECH TREATABILITY
CH231002	ISR-IP PEER REVIEW MANAGEMENT
CH231005	IN SITU MAGNETIC SEPARATION
CH241003	NAPL REMEDIATION USING FOAM
CH331001	REG ISSUES/ASSUMPTIONS ASSOCIATED W/BARRIERS IN VADOSE ZONE
CH341003	MODELING COORDINATION FOR PLUMES FOCUS AREA
MINIMUM ADDITIVE WASTE STABILIZATION	
CH231008	MINIMUM ADDITIVE WASTE STABILIZATION (PLASMA)
CH241002	HIGH TEMPERATURE VITRIFICATION SYSTEMS EVALUATION

OFFICE OF TECHNOLOGY DEVELOPMENT EM-50
FY 1994 ACTIVITIES FUNDED THROUGH THE CHICAGO OPERATIONS OFFICE

(By Program Element)

TTP NUMBER	TITLE
INTERNATIONAL TECHNOLOGY EXCHANGE	
CH223301	RUSSIAN ACTIVITIES
CH244301	INTERNATIONAL SPECIAL PROJECTS
LIAISON AMD COMMUNICATIONS	
CH028001	INSTITUTIONAL & INFORMATION SUPPORT
CH239002	INFORMATION AND COMMUNICATION (EVAL)
PROGRAM DIRECTION	
CH026001	PROGRAM DIRECTION - SALARIES AND OTHER EXPENSES
PROGRAM SUPPORT	
CH025001	TPM SUPPORT
CH125001	TPM SUPPORT
CH225001	TPM SUPPORT
CH325001	TPM SUPPORT
CH525001	TPM SUPPORT
RDDT&E SUPPORT AND NEW INITIATIVES	
CH033501	DIAGNOSTIC INSTRUMENTATION ANALYSIS LABORATORY (DIAL)
CH143501	ELECTROSPRAY MASS SPECTOMETRY
CH201101	HSRC PROGRAM - TECHNICAL SUPPORT
CH201203	REACTIVE METALS TREATMENT
CH333501	NORTHEAST REGIONAL COORDINATION
TECHNOLOGY INTEGRATION	
CH114101	AMES TECH MATURATION PROGRAM
CH144101	EXPEDITED CHARACTERIZATION TECHNOLOGY INTEGRATION SUPPORT
OTHER TECHNOLOGIES - WASTE MINIMIZATION	
CH121202	ELECTROTHERMAL HOLLOW CATHODE
CH242002	STRATEX FOR SOILS
UNDERGROUND STORAGE TANKS ID	
CH232001	TRUEX MODEL VALIDATION
CH243501	MOBILE EVAPORATOR/CONCENTRATOR DEVELOPMENT
EFFICIENT SEPARATIONS AND PROCESSING IP	
CH232004	IN SITU MAGNETICALLY-ASSISTED CHEMICAL SEPARATION
CH232005	ADVANCED PROCESSING FOR CLEAN OPTION
CH232006	AQUEOUS BIPHASIC SYSTEMS/RADIOACTIVE WASTE PRETREATMENT
HAZARDOUS & MIXED WASTE DESTRUCTION IP	
CH232007	PLASMA HEARTH PROCESS RADIOACTIVE WASTE TEST
CH242001	BIO-CATALYTIC DESTRUCTION OF NITRATE + NITRITE
CH242003	PROCESS MONITORING AND CONTROL
CH242004	PHOSPHATE-BONDED CERAMIC WASTE FORMS
CH242005	PHP SLAG CHEMISTRY AND SLAG/METAL PROCESSING
CH321202	POLYMER SOLIDIFICATION
CH332001	WASTE FORM PERFORMANCE CRITERIA
CH342001	MIXED WASTE TREATABILITY-THERMOPLASTIC FINAL FORMS

How to Get Involved with DOE Environmental Management

Section 7.0

7.0 HOW TO GET INVOLVED

WORKING WITH THE DOE OFFICE OF ENVIRONMENTAL MANAGEMENT

DOE provides a range of programs and services to assist universities, industry, and other private-sector organizations and individuals interested in developing or applying environmental technologies. Working with DOE Operations Offices and M&O contractors, EM uses conventional and innovative mechanisms to identify, integrate, develop, and adapt promising emerging technologies. These mechanisms include contracting and collaborative arrangements, procurement provisions, licensing of technology, consulting arrangements, reimbursable work for industry, and special consideration for small business.

Cooperative Research and Development Agreements

EM will facilitate the development of subcontracts, R&D contracts, and cooperative agreements to work collaboratively with the private sector.

EM uses CRADAs as an incentive for collaborative R&D. CRADAs are agreements between a DOE R&D laboratory and any non-Federal source to conduct cooperative R&D that is consistent with the laboratory's mission. The partner may provide funds, facilities, people, or other resources. DOE provides the CRADA partner access to facilities and expertise; however, no Federal funds are provided to external participants. Rights to inventions and other intellectual property are negotiated between the laboratory and participant, and certain data that are generated may be protected for up to 5 years.

Consortia will also be considered for situations where several companies will be combining their resources to address a common technical problem. Leveraging of funds to implement a consortium can offer a synergism to overall program effectiveness.

Procurement Mechanisms

DOE EM has developed an environmental management technology development acquisition policy and strategy that uses phased procurements to span the RDDT&E continuum from applied R&D concept feasibility through full-scale remediation. DOE EM phased procurements make provisions for unsolicited proposals, but formal solicitations are the preferred responses. The principle contractual mechanisms used by EM for industrial and academic response include ROA and PRDA. EM uses the ROA to solicit advanced research and technologies for a broad range of cleanup needs. The ROA supports applied research ranging from concept feasibility through full-scale demonstration. In addition, the ROA is open continuously for a full year following the date of issue and includes a partial procurement set aside for small businesses. Typically, ROAs are published annually in the

Federal Register and the *Commerce Business Daily*, and multiple awards are made.

PRDAs are program announcements used to solicit a broad mix of R&D and DT&E proposals. Typically, a PRDA is used to solicit proposals for a wide-range of technical solutions to specific EM problem areas. PRDAs may be used to solicit proposals for contracts, grants, or cooperative agreements. Multiple awards, which may have dissimilar approaches or concepts, are generally made. Numerous PRDAs may be issued each year.

In addition to PRDAs and ROAs, EM uses financial assistance awards when the technology is developed for public purpose. Financial assistance awards are solicited through publication in the *Federal Register*. These announcements are called Program Rules. A Program Rule can either be a one-time solicitation or an open-ended, general solicitation with annual or more frequent announcements concerning specific funding availability and desired R&D agreements. The Program Rule can also be used to award both grants and cooperative agreements.

EM awards grants and cooperative agreements if fifty-one percent or more of the overall value of the effort is related to a public interest goal. Such goals include possible non-DOE or other Federal agency participation and use, advancement of present and future U.S. capabilities in domestic and international environmental cleanup markets, technology transfer, advancement of scientific knowledge, and education and training of individuals and business entities to advance U.S. remediation capabilities.

Licensing of Technology

DOE contractor-operated laboratories can license DOE/EM-developed technology and software to which they elect to take title. In other situations where DOE owns title to the resultant inventions, DOE's Office of General Counsel will do the licensing. Licensing activities are done within existing DOE intellectual property provisions.

Technical Personnel Exchange Assignments

Personnel exchanges provide opportunities for industrial and laboratory scientists to work together at various sites on environmental restoration and waste management technical problems of mutual interest. Industry is expected to contribute substantial cost-sharing for these personnel exchanges. To encourage such collaboration, the rights to any resulting patents go to the private sector company. These exchanges, which can last from 3 to 6 months, are opportunities for the laboratories and industry to better understand the differing operating cultures, and are an ideal mechanism for transferring technical skills and knowledge.

Consulting Arrangements

Laboratory scientists and engineers are available to consult in their areas of technical expertise. Most contractors operating laboratories have consulting provisions. Laboratory employees who wish to consult can sign non-disclosure agreements, and are encouraged to do so.

Reimbursable Work for Industry

DOE laboratories are available to perform work for industry, or other Federal agencies, as long as the work pertains to the mission of a respective laboratory and does not compete with the private sector.

The special technical capabilities and unique facilities at DOE laboratories are an incentive for the private sector to use DOE's facilities and contractors expertise in this reimbursable work for industry mode. An advanced class patent waiver gives ownership of any inventions resulting from the research to the participating private sector company.

EM Small Business Technology Integration Program

The EM Small Business Technology Integration Program (SB-TIP) seeks the participation of small businesses in the EM Research, Development, Demonstration, Testing and Evaluation programs. Through workshops and frequent communication, the EM SB-TIP provides information on opportunities for funding and collaborative efforts relative to advancing technologies for DOE environmental restoration and waste management applications.

EM SB-TIP has established a special EM procurement set aside for small firms (500 employees or less) to be used for applied research projects, through its ROA. The program also serves as the EM liaison to the DOE Small Business Innovation Research (SBIR) Program Office, and interfaces with other DOE small business offices, as well.

CONTACT

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Environmental Restoration and Waste
Management Technology Development
U.S. Department of Energy
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(301) 903-7940

EM Central Point of Contact

The EM Central Point of Contact is designed to provide ready access to prospective research and business opportunities in waste management, environmental restoration, and decontamination and decommissioning activities, as well as information on EM-50 Ips and Ids. The EM Central Point of Contact can identify links between industry technologies and program needs, and provides potential partners with a connection to an extensive complex-wide network of DOE Headquarters and field program contacts.

The EM Central Point of Contact is the best single source of information for private-sector technology developers looking to collaborate with EM scientists and engineers. It provides a real-time information referral service to expedite and monitor private-sector interaction with EM.

To reach the EM Central Point of Contact, call 1-800-845-2096 during normal business hours (Eastern time).

Office of Research and Technology Applications

Office of Research and Technology Applications serve as technology transfer agents at the Federal laboratories, and provide an internal coordination in the laboratory for technology transfer and an external point of contact for industry and universities. To fulfill this dual purpose, ORTAs license patents and coordinate technology transfer activities for the laboratory's scientific departments. They also facilitate one-on-one interactions between the laboratory's scientific personnel and technology recipients, and provide information on laboratory technologies with potential applications in private industry for state and local governments.

For more information about these programs and services, please contact:

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Acronym Listing

Section 8.0

8.0 ACRONYMS

ABS	aqueous biphasic separation
ANL	Argonne National laboratory
AOTF	acousto-optic tunable filter
AP TOF	associated-particle time-of-flight (technique)
BNL	Brookhaven National Laboratory
CAA	Contaminant Analysis Automation
CAD	computer-aided design
CARS	Coherent Anti-Stokes Raman Spectrometers
CE	capillary electrophoresis
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CPT	cone penetrometer truck
CRADA	Cooperative Research and Development Agreement
CTET	carbon tetrachloride
CWL	Chemical Waste Landfill
D&D	Decontamination and Dismantlement
DIAL	Diagnostic Instrumentation and Analysis Laboratory
DNAPLS	dense non-aqueous phase liquids
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
ECM	Environmentally Conscious Manufacturing
ECPT	electric cone penetrometer
EM	Office of Environmental Restoration and Waste Management
EMS	electrospray mass spectrometry
EPA	U.S. Environmental Protection Agency
ESC	Expedited Site Characterization
ET	emerging technologies
FEMP	Fernald Environmental Management Project
FFCA	Federal Facility Compliance Agreement
FFP	finesse fiber-optic Fabry-Perot (interferometer)
FTIR-PAS	Fourier-transform infrared photoacoustic spectroscopy
FUSRAP	Formerly Utilized Sites Remedial Action Program
FY	fiscal year
GC	gas chromatograph
GISs	Geographical Information Systems
GTM	Generic TRUEX Model
HLW	High-Level Waste
ICP-MS	inductively coupled plasma-mass spectrometer
IDs	Integrated Demonstrations
IIA	Innovation Investment Area

INEL	Idaho National Engineering Laboratory
IPs	Integrated Programs
LA	laser ablation
LA-ICP-AES	laser ablation inductively coupled plasma - atomic emission spectroscopy
LANL	Los Alamos National Laboratory
LIF	Laser-Induced Fluorescence
LLNL	Lawrence Livermore National Laboratory
LOGS	Laser Optogalvanic Spectrometers
MACS	magnetically-assisted chemical separation
MAWS	Minimum Additive Waste Stabilization Program
MDL	minimum detectable level
MDLEST	mobile demonstration laboratory for environmental screening technologies
METC	Membrane and Carbon Adsorption
MISC	Minimally Invasive Three-Dimensional Site Characterization
MLLW	Mixed, Low-level waste
MS	mass spectrometer
MWIP	Mixed Waste Integrated Program
MWLID	Mixed Waste Landfill Integrated Demonstration
MWO	Mixed Waste Operations
NAPLs	nonaqueous phase liquids
NPL	National Priorities List
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
OTD	Office of Technology Development
PAH	polycyclic aromatic hydrocarbon
PCBs	polychlorinated biphenyls
PE/AS	potassium emission/absorption system
PGRS	Passive Gamma-Ray Spectroscopy
PNC	Power Reactor and Nuclear Fuel Development Corporation
PNL	Pacific Northwest Laboratory
PRDA	Program Research and Development Announcement
PVC	poly-vinyl chloride
QCMs	quartz crystal microbalances
RCRA	Resource Conservation and Recovery Act
R&D	research and development
RDDT&E	Research and Development, Demonstration, Testing, and Evaluation
RDBSs	Relational Database Systems
ROAs	Research Opportunity Announcement
ROD	Record of Decision
RTDP	Robotics Technology Development Program
SAW	surface-acoustic-wave
SCAPS	Site Characterization and Analysis Penetrometer System
SEAMIST^{SM}	Science and Engineering Associates Membrane Instrumentation and Sampling Technique

SEAR	surfactant-enhanced aquifer remediation
SITE	Superfund Innovative Technology Evaluation program
SLAPS	St. Louis Airport Site
SNL	Sandia National Laboratory
SOPT	state-of-the-practice
SREX	Strontium Extraction Process
SRS	Savannah River Site
SST	single-shell tank
STNG	sealed-tube neutron generator
SVOCs	semi-volatile organic compounds
TBP	tributyl phosphate
TCE	trichloroethylene
TCLP	Toxicity Characteristic Leaching Procedure
TFRs	thin film resonators
TIP	Technology Integrated Program
TIRS	transient infrared spectroscopy
TRU	transuranic
TRUEX	Transuranic Element Extraction Process
TSCA	Toxic Substances Control Act
TTPs	Technical Task Plans
TWO	Tank Waste Retrieval
UMTRA	Uranium Mill Tailings Remedial Action
USTs	underground storage tanks
UV	ultraviolet
VOCs	volatile organic compounds
WIPP	Waste Isolation Pilot Plant
ZTLs	zero-tension lysimeters