



# **RADIOACTIVE TANK WASTE REMEDIATION FOCUS AREA**

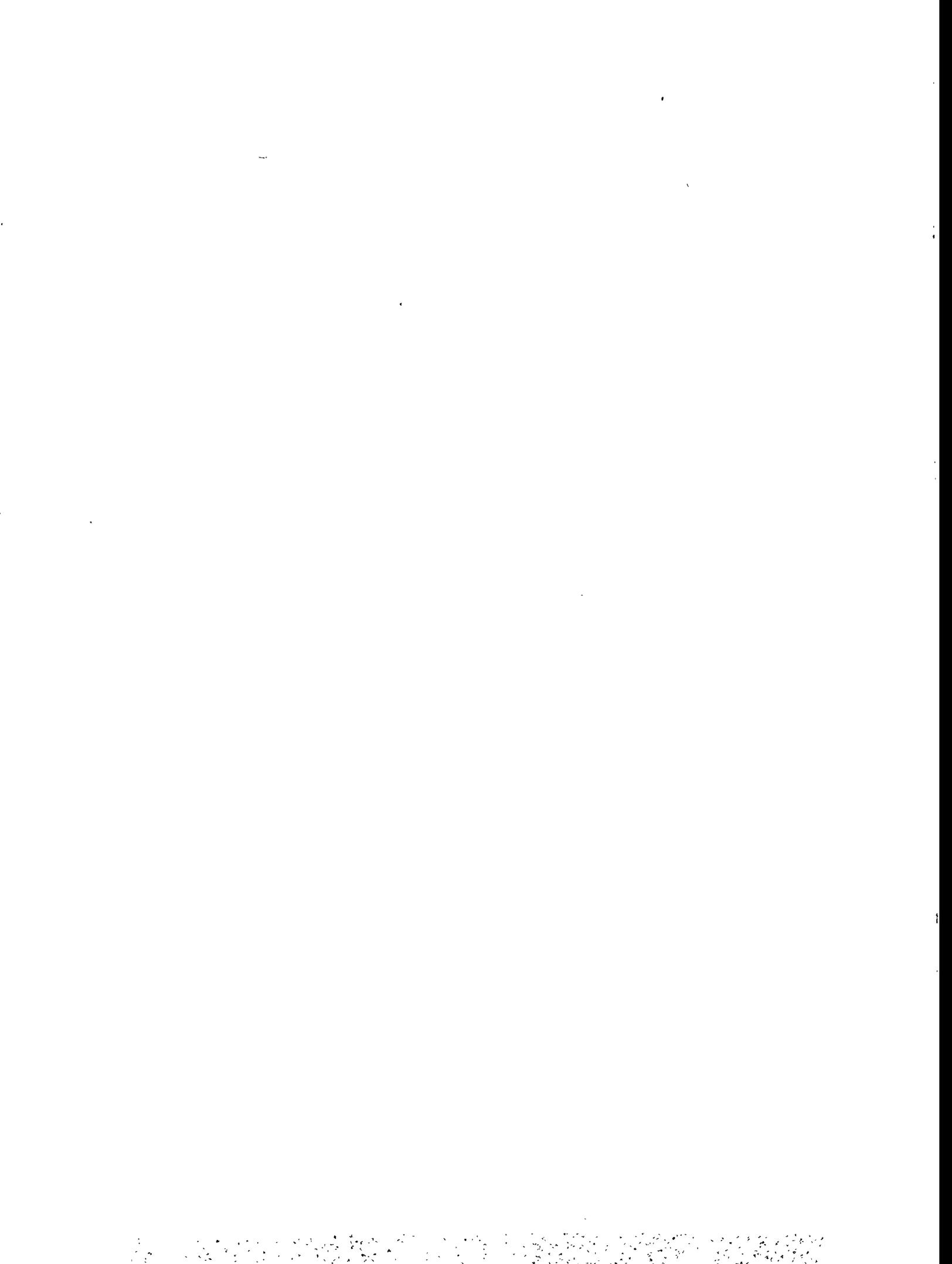
**Technology Summary  
August 1996**

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# RADIOACTIVE TANK WASTE REMEDIATION FOCUS AREA TECHNOLOGY SUMMARY

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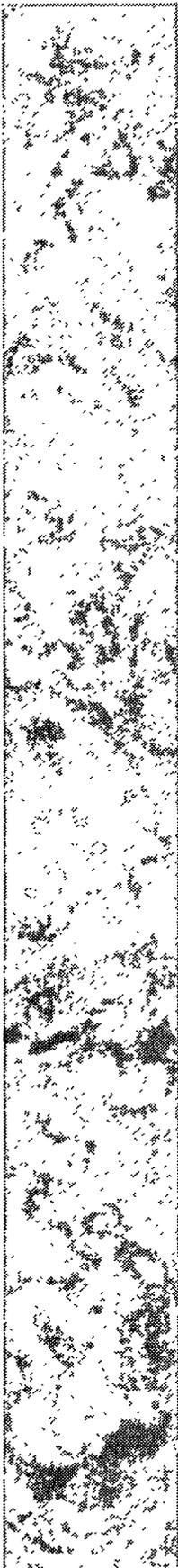


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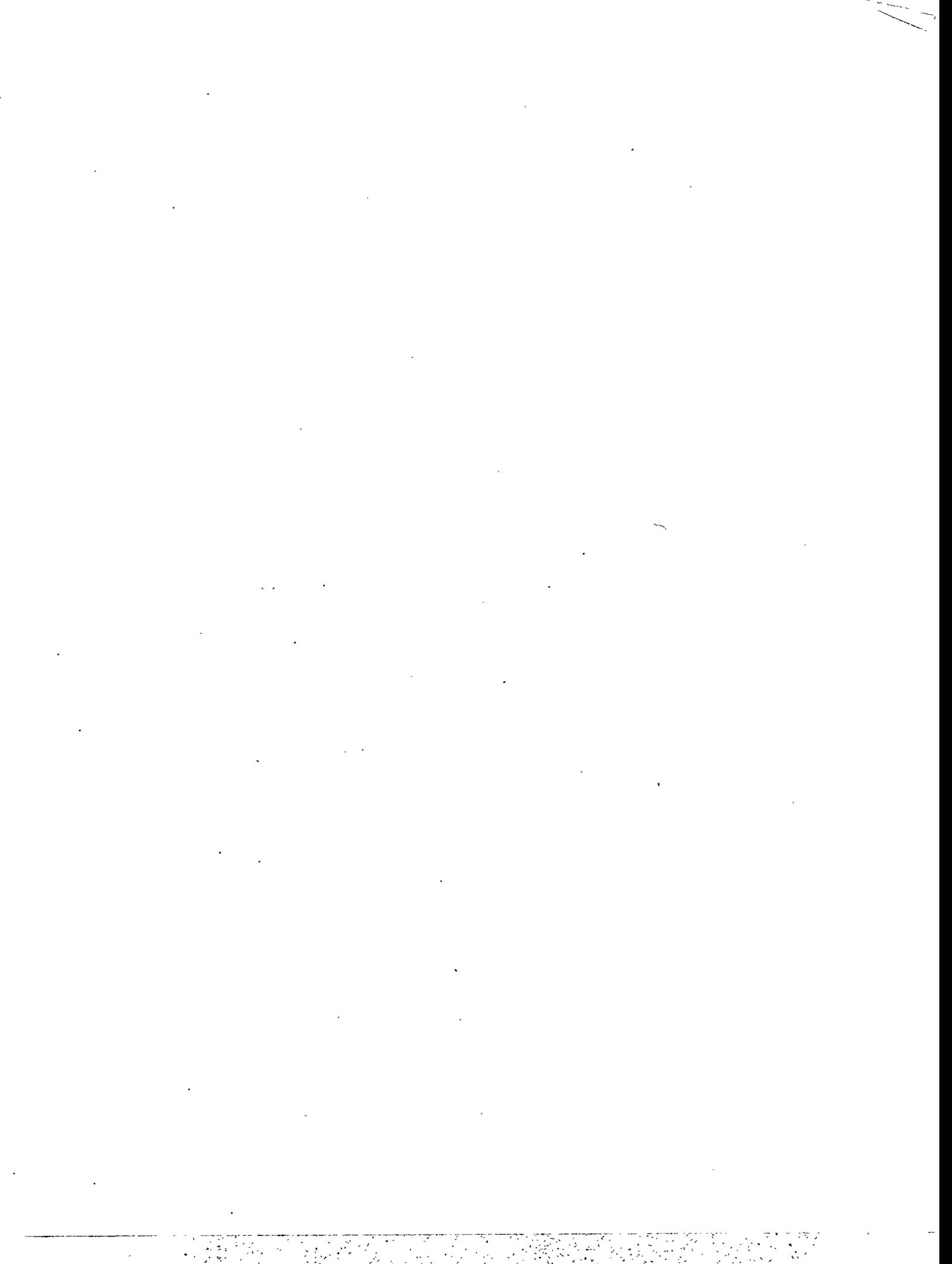
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## INTRODUCTION

The Office of Environmental Management (EM) is responsible for cleaning up the legacy of radioactive and chemically hazardous waste at contaminated sites and facilities throughout the U.S. Department of Energy (DOE) nuclear weapons complex, preventing further environmental contamination, and instituting responsible environmental management. Initial efforts to achieve this mission resulted in the establishment of environmental restoration and waste management programs. However, as EM began to execute its responsibilities, decision makers became aware that the complexity and magnitude of this mission could not be achieved efficiently, affordably, safely, or reasonably with existing technology.

Once the need for advanced cleanup technologies became evident, EM established an aggressive, innovative program of applied research and technology development. The Office of Technology Development (OTD) was established in November 1989 to advance new and improved environmental restoration and waste management technologies that would reduce risks to workers, the public, and the environment; reduce cleanup costs; and devise methods to correct cleanup problems that currently have no solutions.

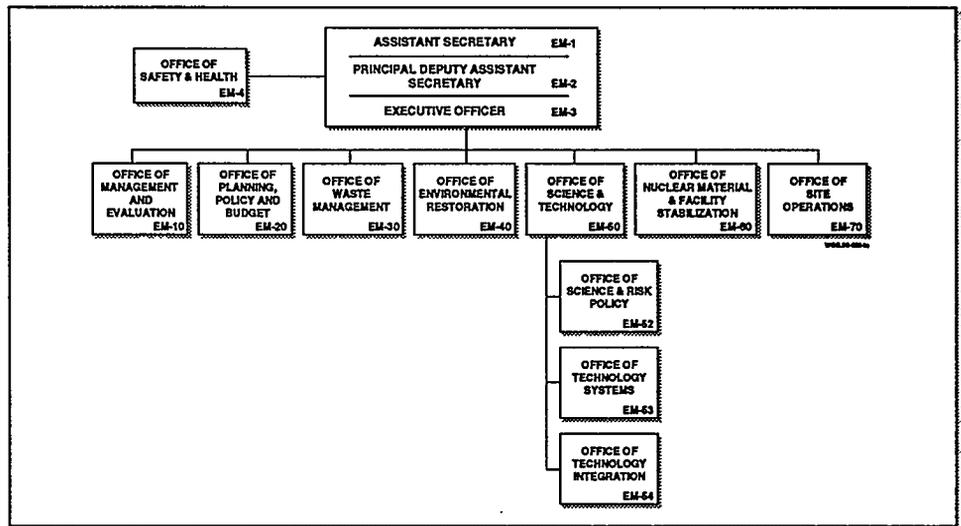
In 1996, OTD added two new responsibilities—management of a Congressionally mandated environmental science program and development of risk policy, requirements, and guidance. OTD was renamed the Office of Science and Technology (OST).

### THE EM ORGANIZATION

OST is one of seven Deputy Assistant Secretarial Offices within EM. Each Deputy Assistant Secretarial Office is discussed here, with the exception of OST (EM-50), addressed in detail later in this Introduction.

#### **Office of the Assistant Secretary for Environmental Management (EM-1)**

The Office of the Assistant Secretary for Environmental Management provides centralized direction for waste management operations, environmental restoration, and related applied research and development programs and activities within DOE. The Office of the Assistant Secretary develops EM program policy and guidance for the assessment and cleanup of inactive waste sites and facilities, and waste management operations; develops and implements an applied waste research and development program to provide innovative environmental technologies to yield permanent disposal solutions at reduced costs; and oversees the transition of contaminated facilities from various departmental programs to environmental restoration. The Assistant Secretary provides guidance to all DOE Operations Offices. Organizational relationships are shown in Figure A.



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**Figure A.** Office of Environmental Management Organization Chart

**The Office of Management and Evaluation (EM-10)**

The Deputy Assistant Secretary for Management and Evaluation serves as the Assistant Secretary’s principal advisor on all administrative functions and activities for EM line offices. Responsibilities include personnel administration; training and career development; total quality management; organization and manpower management; cost and performance management; space and logistics management; acquisition, procurement, and contracts management; general administrative support services; and automated data processing, automated office support systems, and information resources management.

**The Office of Planning, Policy, and Budget (EM-20)**

The Office of Planning, Policy, and Budget analyzes and provides support on policy and planning issues associated with environmental compliance and cleanup activities, waste management, nuclear materials and facilities stabilization, overall budget and priority setting analyses, nuclear nonproliferation policy practices, and the ultimate disposition of surplus materials and facilities. This Office is also responsible for the review, coordination, and integration of inter-site, interagency and international planning activities related to these issues. The Office coordinates policy and procedural issues associated with the external regulation of the environmental restoration, waste management, and nuclear materials and facility stabilization programs.

**The Office of Waste Management (EM-30)**

The Office of Waste Management provides an effective and efficient system that minimizes, treats, stores, and disposes of DOE waste as soon as possible in order to protect people and the environment from the hazards of those wastes. The Office carries out program planning and budgeting, evaluation and intervention, and representation functions associated with management

of radioactive high-level, transuranic, and low-level waste; hazardous and sanitary waste; and mixed waste.

#### **The Office of Environmental Restoration (EM-40)**

The Office of Environmental Restoration remediates departmental sites and facilities to protect human health and the environment from the risks posed by inactive and surplus DOE facilities and restores contaminated areas for future beneficial use. This Office provides program direction for and management of environmental restoration activities involving inactive sites and facilities, including the decontamination of surplus facilities.

#### **The Office of Nuclear Material and Facility Stabilization (EM-60)**

The Nuclear Material and Facility Stabilization program mission is to protect people and the environment from the hazards of nuclear materials and to deactivate surplus facilities in a cost-effective manner. The Office provides program planning and budgeting, evaluation and intervention, and representation functions associated with the stabilization of nuclear materials and the deactivation of surplus facilities.

#### **The Office of Site Operations (EM-70)**

Acting to eliminate barriers and ensure that field concerns are recognized in major EM decisions, the Office of Site Operations acts as a focal point and champion for the Operations Offices and field sites, serving as facilitator, coordinator and ombudsman for crosscutting issues and topics raised by the various EM elements. The Office of Site Operations provides Headquarters policy direction for landlord planning and budgeting and sets policy and guidance to improve the effectiveness of crosscutting environment, transportation management, and waste minimization activities.

### **THE OFFICE OF SCIENCE AND TECHNOLOGY (EM-50)**

OST manages and directs focused, solution-oriented national technology development programs to support EM by using a systems approach to reduce waste management life-cycle costs and risks to people and the environment. OST programs involve research, development, demonstration, testing, and evaluation of innovative technologies and technology systems that meet end-user needs for regulatory compliance. Activities include coordination with other stakeholders and the private sector, as well as collaboration with international organizations. In 1994, the EM program identified five major problem areas on which to focus its technology development activities (later two were combined), and implemented Focus Areas to address these problems. In addition, some needs were identified that were common to all the Focus Areas, and three Crosscutting Programs were created to address them.

OST programs establish, manage, and direct targeted, long-term research programs to bridge the gap between broad fundamental research that has

wide-ranging application and needs-driven applied technology development research. OST expects to produce technologies to answer the needs of its major customers within EM for innovative science and technology through

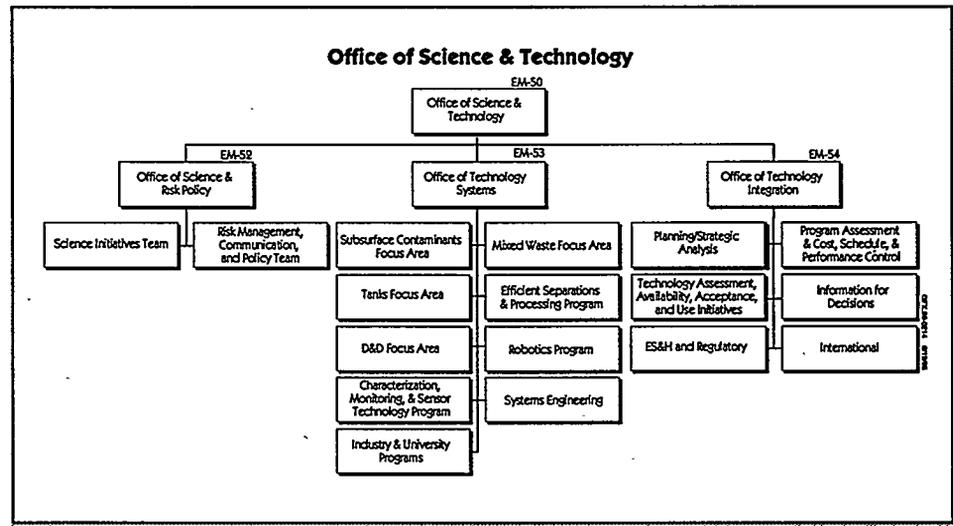


Figure B. Organization Chart of the Office of Science and Technology

integration of basic research programs, applied research programs (Focus Areas and Crosscutting Programs), industry partnerships, and technology transfer activities.

Three offices comprise OST: the Office of Science and Risk Policy, the Office of Technology Systems, and the Office of Technology Integration. The organization for OST is shown in Figure B.

## OFFICE OF SCIENCE AND RISK POLICY (EM-52)

The Office of Science and Risk Policy manages EM's Science Program and the formulation of risk policy. The mission of this office includes the development of a targeted, long-term basic research agenda for environmental problems so that "transformational" or breakthrough approaches can lead to significant reduction in the costs and risks associated with the EM Program. This Office also bridges the gap between broad fundamental research that has wide-ranging applicability, such as that performed in DOE's Office of Energy Research, and needs-driven applied technology development that is conducted in EM's Office of Technology Systems. This Office was designed to focus the country's science infrastructure on critical national environmental management problems.

The Science Program draws on information from its DOE customers to identify necessary basic research. The Science Program concentrates its efforts on the characterization of DOE's wastes and contaminants, interactions of

radioactive elements with biosystems in various natural media and waste forms, extraction and separation of radioactive and hazardous chemical contaminants, prediction and measurement of contaminant movement in DOE facilities' environments, and formulation of scientific bases for the risks associated with DOE-based contaminants.

Risk policy activities within this Office involve the development of policies, procedures, and guidance to ensure that EM activities in preventing risks to the public, workers, and the environment are within prescribed, acceptable levels. Risk evaluation methods and event and consequence analyses provide DOE with a basis for assessing both the risk and any actions being considered to reduce that risk. The Office of Science and Risk Policy ensures that advances in risk evaluation methods are integrated into coherent decision-making processes regarding risk acceptability. Decision-making processes must meet DOE missions while protecting public health, worker health and safety, ecosystem viability, and cultural and national resources.

### **OFFICE OF TECHNOLOGY SYSTEMS (EM-53)**

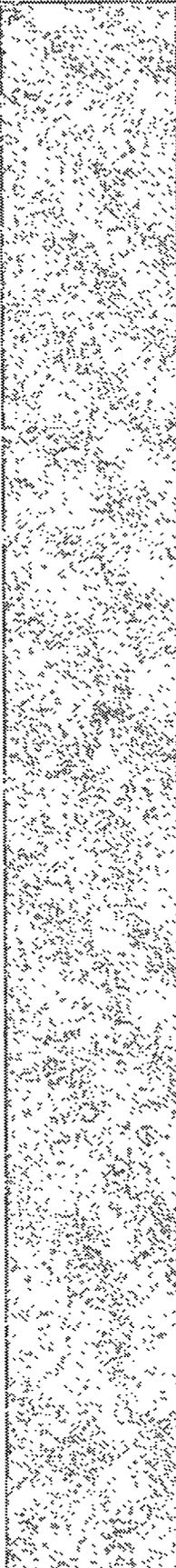
OST programs involve research, development, demonstration, testing, and evaluation activities designed to produce innovative technologies and technology systems to meet national needs for regulatory compliance, lower life-cycle costs, and reduced risks to the environment. To optimize resources, OST has streamlined technology management activities into a single focus team for each major problem area. To ensure programs are based upon user needs, these teams include representatives from user offices within EM. There are four major problem areas upon which technology development activities are focused.

- Mixed Waste Characterization, Treatment, and Disposal
- Radioactive Tank Waste Remediation
- Subsurface Contaminants
- Decontamination and Decommissioning

#### **Mixed Waste Characterization, Treatment, and Disposal Focus Area**

DOE stores 167,000 cubic meters of mixed low-level and transuranic waste from over 1,400 mixed radioactive and hazardous waste streams at 38 sites. The Mixed Waste Characterization, Treatment, and Disposal Focus Area provides an integrated, multi-organizational, national team to develop treatment systems for the department's inventory of mixed radioactive and hazardous waste and to dispose of these low-level and transuranic waste streams in a manner that fulfills regulatory requirements.

This Focus Area plans to demonstrate three technologies to treat at least 90 percent of DOE's stored mixed waste inventory by the end of FY97. The



outcome will be waste forms that are reduced in volume, as compared to the volume of stored mixed waste, and meet regulatory requirements for safe, permanent disposal. Technology development is being conducted in the areas of thermal and nonthermal treatment emissions, nonintrusive drum characterization, material handling, and final waste forms.

#### **Radioactive Tank Waste Remediation Focus Area**

The Radioactive Tank Waste Remediation Focus Area develops technologies to safely and efficiently remediate over 300 underground storage tanks that have been used to process and store more than 90 million gallons of high-level radioactive and chemical mixed waste. Technologies are needed to characterize, retrieve, and treat the waste before radioactive components are immobilized. All this must be done in a safe working environment. Emphasis is placed on in situ or remotely handled processes and waste volume minimization.

Research and development of technologies in this area is aimed at enabling tank farm closure using safe and cost-efficient solutions that are acceptable to the public and that fulfill Federal Facility Compliance Act requirements of site regulatory agreements.

#### **Subsurface Contaminants Focus Area**

The Subsurface Contaminants Focus Area is developing technologies to address environmental problems associated with hazardous and radioactive contaminants in soil and groundwater that exist throughout the DOE complex, including radionuclides, heavy metals, and dense, nonaqueous phase liquids. More than 5,700 known DOE groundwater plumes have contaminated over 600 billion gallons of water and 50 million cubic meters of soil. Migration of these plumes threatens local and regional water sources, and in some cases has already adversely impacted off-site resources. In addition, the Subsurface Contaminants Focus Area is responsible for supplying technologies for the remediation of numerous landfills at DOE facilities. These landfills are estimated to contain over 3 million cubic meters of radioactive and hazardous buried waste, some of which has migrated to the surrounding soils and groundwater. Technology developed within this specialty area will provide effective methods to contain contaminant plumes and new or alternative technologies for remediating contaminated soils and groundwater. Emphasis is placed on the development of in situ technologies to minimize waste disposal costs and potential worker exposure by treating plumes in place. While addressing contaminant plumes emanating from DOE landfills, the Subsurface Contaminants Focus Area is also working to develop new or alternative technologies for the in situ stabilization and nonintrusive characterization of these disposal sites.

#### **Decontamination and Decommissioning Focus Area**

The Decontamination and Decommissioning Focus Area is developing technologies to solve the department's challenge of deactivating 7,000

contaminated buildings and decommissioning 700 contaminated buildings. It is also responsible for decontaminating the metal and concrete within those buildings and disposing of 180,000 metric tons of scrap metal. Technology development for decontamination and decommissioning focuses on large-scale demonstrations, each of which incorporates improved technologies identified as responsive to high-priority needs. All technologies will be considered for eventual deployment, and side-by-side comparisons of improved technologies are being performed using existing commercial technologies as baselines.

## CROSSCUTTING PROGRAMS

In addition to work directed to specific Focus Areas, EM is engaged in research and development programs that cut across these problem areas. Technologies from these Crosscutting Programs may be used within two or more of the Focus Areas to help meet program goals. These programs complement and facilitate technology development in the Focus Areas as shown in Figure C. The Crosscutting Programs are:

- Characterization, Monitoring, and Sensor Technologies,
- Efficient Separations and Processing, and
- Robotics Technology Development Program.

### Characterization, Monitoring, and Sensor Technologies Crosscutting Program

DOE is required to characterize more than 3,700 contaminated sites, 1.5 million barrels of stored waste, 385,000 m<sup>3</sup> of high-level waste in tanks, and from 1,700 to 7,000 facilities before remediation, treatment, and facility transitioning commence. Monitoring technologies are needed to ensure worker safety and effective cleanup during remediation, treatment, and site closure.

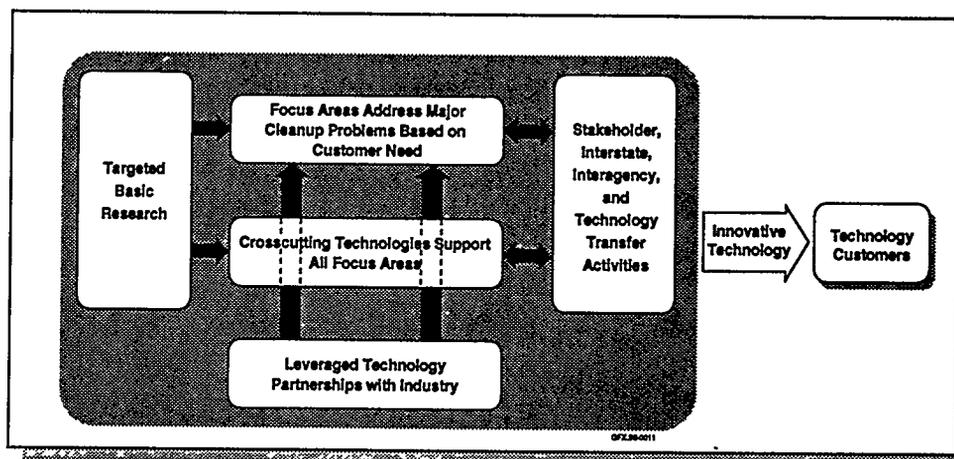


Figure C. Relationships between Focus Areas and Crosscutting Programs

### **Efficient Separations and Processing Crosscutting Program**

Separations and selected treatment processes are needed to treat and immobilize a broad range of radioactive wastes. In some cases, treatment technologies do not exist; in others, improvements are needed to reduce costs and secondary waste volumes and to improve waste form quality. This Crosscutting Program concentrates efforts on specific high-priority needs as defined by the Focus Areas, then evaluates and adapts the technologies for other applicable Focus Areas.

This program is working to meet Federal Facilities Compliance Act milestones and other regulatory requirements, and to develop separations and treatment technologies that minimize risk, the volume of waste requiring deep, geological disposal, and secondary waste volumes.

### **Robotics Technology Development Crosscutting Program**

Existing technologies are often inadequate to meet EM's mission needs both at a reasonable cost and under conditions that promote adequate worker safety. Robotic systems reduce worker exposure to the absolute minimum while providing proven, cost-effective, and, in some cases, the only acceptable approach to problems.

Robotics remote systems development work occurs in three areas. Remote systems for decontamination and dismantlement of facilities will reduce or eliminate extensive worker radiation protection requirements and increase productivity. Robotic systems for characterization and retrieval of stored tank waste will allow work to proceed within the radiation fields in the waste storage area. Automated chemical/radiological analysis systems are estimated to provide a cost benefit of \$10.5 billion from FY96 through FY00.

## **INDUSTRY AND UNIVERSITY PROGRAMS**

Industry and University programs provide to the Focus Areas and the Crosscutting Programs the capability to involve private industry, universities, and other interested parties in their program through direct procurement with DOE. The public-private partnerships that are established encourage the enhancement and commercialization of technologies developed by the private sector through pilot- and field-scale demonstration at DOE sites. The integration of industry, academia, and the DOE laboratories allows all aspects of the technology to be evaluated, including worker safety and health, commercial potential, and technical merit.

Industry and University activities support more than 100 agreements with the private sector. These agreements include the Small Business Innovative Research (SBIR) program, international activities, stakeholder activities, worker safety and health activities, and commercialization initiatives, as well as the direct support to the Focus Areas. For information on how to participate in

these programs, see the "DOE Business Opportunities" section at the end of this book.

### **OFFICE OF TECHNOLOGY INTEGRATION (EM-54)**

The Office of Technology Integration addresses issues that affect the involvement of critical external entities such as production/waste sites, users, the public, tribes, regulators, and commercial parties. The office is involved in the assessment, acceptability, availability, and use of improved technical solutions by providing uniform guidance, tools, and initiatives to support the Office of Technology Systems. This office also sponsors efforts to encourage and promote the involvement of affected parties' in regulatory issues.

In addition, the Office of Technology Integration sponsors domestic and international technology transfer programs within OST and coordinates planning and cost-benefit analyses with other EM organizations.

# RADIOACTIVE TANK WASTE REMEDIATION FOCUS AREA OVERVIEW

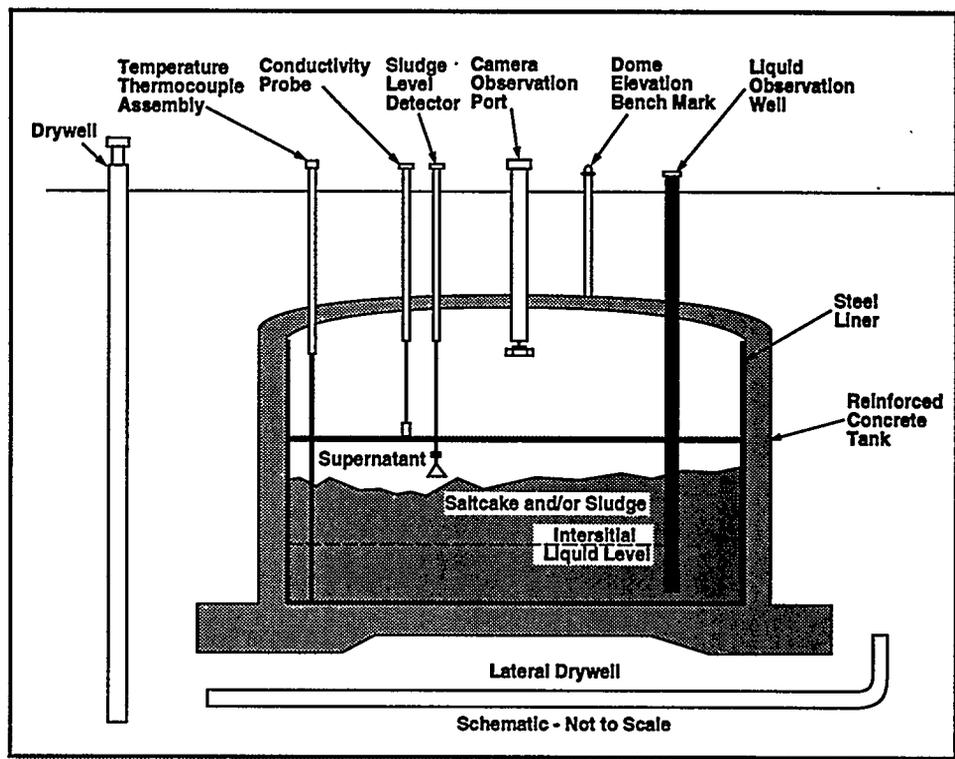
## THE CHALLENGE

EM's Office of Science and Technology has established the Tank Focus Area (TFA) to manage and carry out an integrated national program of technology development for tank waste remediation. The TFA is responsible for the development, testing, evaluation, and deployment of remediation technologies within a system architecture to characterize, retrieve, treat, concentrate, and dispose of radioactive waste stored in the underground storage tanks at Department of Energy (DOE) facilities and ultimately stabilize and close the tanks. The goal is to provide safe and cost-effective solutions that are acceptable to both the public and regulators.

Within the DOE complex, 335 underground storage tanks have been used to process and store radioactive and chemical mixed waste generated from weapon materials production and manufacturing. Collectively, these tanks hold over 90 million gallons of high-level and low-level radioactive liquid waste in sludge, saltcake, and as supernate and vapor. Very little has been treated and/or disposed of in final form.

Tanks vary in design from carbon or stainless steel to concrete, and concrete with carbon steel liners. Two types of storage tank are most prevalent: the single-shell and double-shell concrete tanks with carbon steel liners (see Figure D). Capacities vary from 5,000 gallons (19 m<sup>3</sup>) to 1,300,000 gallons (4,920 m<sup>3</sup>). The tanks are covered with a layer of soil ranging from a few feet to tens of feet thick.

Most of the waste is alkaline and contains a diverse portfolio of chemical constituents including nitrate and nitrite salts (approximately half of the total waste), hydrated metal oxides, phosphate precipitates, and ferrocyanides. The 784 MCI (see Figure E) of radionuclides are distributed primarily among the transuranic (TRU) elements and fission products, specifically strontium-90, cesium-137, and their decay products yttrium-90 and barium-137. In-tank atmospheric conditions vary in severity from near ambient to temperatures over 93°C. Tank void-space radiation fields can be as high as 10,000 rad/h.



**Figure D.** This typical single wall tank is one of the most prevalent tank designs.

The TFA has focused its attention on four DOE locations:

- Hanford Site near Richland, Washington
- Idaho National Engineering Laboratory (INEL) near Idaho Falls, Idaho
- Oak Ridge Reservation near Oak Ridge, Tennessee
- Savannah River Site (SRS) near Aiken, South Carolina

Hanford has 177 tanks that contain approximately 55 million gallons of hazardous and radioactive waste. There are 149 single-shell tanks that have exceeded their life expectancy. Sixty-seven of these tanks have known or suspected leaks. Due to several changes in the production processes since the early 1940s, some of the tanks contain incompatible waste components, generating hydrogen gas and excess heat that further compromise tank integrity.

Tank Characteristics	Sites			
	Hanford	INEL	Oak Ridge	SRS
No. of tanks	177	11 (tanks) 7 (calcine vaults)	56 (inactive) 13 (active) 27 (collection tanks)	51
Waste Volume (million gallons)	55	2 (tanks) 1 (calcine vaults)	0.5 (legacy) 0.4 (active/year)	33
Activity (MCi)	198	2 (tanks) 50 (calcine vaults)	0.13 (legacy) 0.034 (active)	534

**Figure E.** Tank Summary for Hanford, INEL, Oak Ridge, and SRS

The 11 stainless steel tanks at INEL store approximately 2 million gallons of acidic liquids. Calcine is stored in seven stainless steel bins enclosed in massive underground concrete vaults. Most of the INEL wastes are calcined solids.

Dilute low-level waste (LLW) supernatants and associated sludges at the Oak Ridge Reservation are stored in the inactive Gunitite and associated tanks (GAATs), the old hydrofracture tanks, and other tanks. The wastes from an underground collection system are sent to stainless steel central treatment/storage tanks, including eight Melton Valley Storage Tanks (MVSTs).

Tank waste at SRS consists of 33 million gallons of salt, salt solution, and sludge containing waste stored in 51 underground storage tanks. Twenty-three tanks are being retired, because they do not have full secondary containment. Nine tanks have leaked detectable quantities of waste from the primary tank to secondary containment.

The TFA has focused its technology development in areas where currently available technology does not meet technical and safety requirements for tank waste remediation and where significant reduction in life-cycle cost can be achieved. Most of the participant sites share four problem functional areas comprising the elements of the TFA technical program. These functional areas are:

- Characterization and Safety
- Retrieval and Tank Closure
- Pretreatment
- Waste Immobilization and Disposal

This document presents technology summaries in these four functional areas.

Historically, characterization of tank waste has been very expensive, has failed to obtain representative data for many tanks, and has generated safety concerns from worker exposure to radioactive waste. Within the Characterization and Safety functional area, the TFA is developing systems to identify chemical and physical characteristics of the waste inside the tank, improve data quality and timeliness, and reduce safety concerns. Laser ablation/mass spectroscopy (LA/MS) and near infrared (NIR) spectroscopy are examples of waste analysis systems in development. The LA/MS will be deployed in FY96 at the Hanford site. The NIR spectroscopy system was deployed in early FY96 in a Hanford production hot cell to analyze moisture content on core samples.

The TFA is developing waste retrieval devices capable of dislodging the sludge and saltcake fractions of the wastes and conveying them from the tanks that can be deployed with remotely controlled robotic arms and vehicles. These devices are designed to fit through 12-inch diameter access ports, and to work in highly radioactive environments. The Confined Sluicing End Effector prototype successfully retrieved simulated sludge in the Hydraulic Test Bed at the Hanford Site in February 1996. This end effector will be deployed with the Modified Light Duty Utility Arm (MLDUA) at Oak Ridge in FY97.

The Waste Retrieval and Tank Closure functional area is demonstrating cost-efficient methods to remove saltcake and waste heels and close a high-level waste tank. Savannah River and Hanford have numerous tanks that contain saltcake so that the potential cost savings of less expensive saltcake retrieval methods is very large. The alternate saltcake dissolution method to be implemented is the Modified Density Gradient Method. Additionally, a borehole miner is being used to break up the tank heel.

Pretreatment techniques will separate tank wastes into low- and high-level fractions, thereby significantly reducing the volumes of high-level waste requiring disposal. Successes in pretreatment have included design of a Cesium Removal Demonstration (CsRD) unit and a mobile evaporator to concentrate tank waste. Construction of the CsRD unit is underway using state-of-the-art ion-exchange materials developed by the Efficient Separations and Processing Crosscutting Program. Cesium-loaded separations media from the CsRD will also be treated and vitrified in another task within the Waste Immobilization functional area. An Out-of-Tank Evaporator Demonstration will begin in FY96.

LLW immobilization will reduce waste volumes and produce waste forms that are chemically and physically durable. The TFA is applying two technologies (grout and glass) to the same waste stream to allow an unbiased appraisal of the true costs and risks associated with implementing each technology for full-scale tank waste remediation.

The TFA secures the active involvement of private industry, universities, and other government agencies through establishing collaborative partnerships [e.g., Cooperative Research and Development Agreements (CRADAs)], licensing of technologies, fostering technical personnel exchanges, effecting consulting agreements, and prompting shared use of scientific facilities. The TFA technology development program seeks to reflect the issues and concerns of stakeholders, including regulators and technology users at each of the sites through the Site Technology Coordination Groups, the site-specific advisory boards, and the Community Leaders Network.

A number of the technologies developed under the TFA will be transferrable to other applications outside the DOE complex. Newly developed characterization technologies will be used in tanks and pipes containing materials other than radioactive mixed waste. The retrieval technologies developed may contribute to automation-assisted manufacturing, nonradioactive waste management, underwater mining and retrieval operations, and nuclear power plant operations.

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## 1.0

# CHARACTERIZATION AND SAFETY OVERVIEW

DOE, contractors, and stakeholders have committed to a safe and efficient remediation of high-level waste (HLW), mixed waste, and hazardous waste stored in underground tanks across the DOE complex. The Office of Science and Technology has undertaken the task of developing technologies for safe, expedient, and cost-effective remediation of HLW in tanks. The Tank Focus Area (TFA) is developing and deploying technologies which focus on HLW tank remediation.

Currently, there are no fully developed or deployed in situ techniques to characterize tank waste. In situ characterization can eliminate the time delay between sample removal and sample analysis and aid in guiding the sampling process while decreasing the cost (approximately \$1 million is spent for one tank core extrusion) of waste analysis. Most importantly, remote analysis eliminates sample handling and safety concerns due to worker exposure. However, analysis of extruded tank samples allows a more complete chemical and physical characterization of the waste when needed.

Knowledge of the chemical and radioactive composition and physical parameters of the waste is essential to safe and effective tank remediation. The TFA is developing technologies that identify chemical species in liquid, sludge, and solids within the confines of a tank and in samples that are removed from the tanks. The TFA is also developing a system for tank leak detection. The sensors under development will be capable of being used in a safely controlled environment, i.e., hot cell facilities, placed around the tank wall boundaries or deployed directly inside a tank.

To meet the demands, the TFA is developing a laser Raman method for in situ molecular chemical analysis, a hot cell laser ablation/mass spectrometry system for isotopic analysis, and a near infrared spectroscopic system for moisture content analysis within the hot cell facilities. An electrical resistance tomography system is being developed for tank leak detection.

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# 1.1

## ADVANCE HOT CELL ANALYTICAL TECHNOLOGY - LASER ABLATION/MASS SPECTROSCOPY

### TECHNOLOGY NEED

There are three primary drivers for the development of new chemical analysis methods to support tank waste remediation: 1) provide analyses for which there are currently no reliable existing methods, 2) replace current methods that require too much time and/or are too costly, and 3) provide methods that evolve into on-line process analysis tools for use in waste processing facilities.

Characterization of the elemental and isotopic chemical constituents in DOE tank waste is an important function in support of DOE tank waste operation and remediation functions. Proper waste characterization enables: safe operation of the tank farms; resolution of tank safety questions; and development of processes and equipment for retrieval, pretreatment, and immobilization of tank waste. All of these operations are dependent on the chemical analysis of tank waste.

### TECHNOLOGY DESCRIPTION

Laser Ablation/Mass Spectroscopy (LA/MS) provides elemental and/or isotopic detection and quantification of most elements in the periodic table (see Figure 1.1-1). As illustrated in Figure 1.1-2 the LA/MS uses a system consisting of a pulsed laser for sample ablation, a gas flow transfer system for sample transport, and an inductively coupled plasma/mass spectrometer (ICP/MS) for chemical separation and analysis. The laser produces energetic optical pulses suitable for ablating materials from a sample. The ablated sample plume is extracted and transferred by the carrier gas (argon) to the ICP torch where

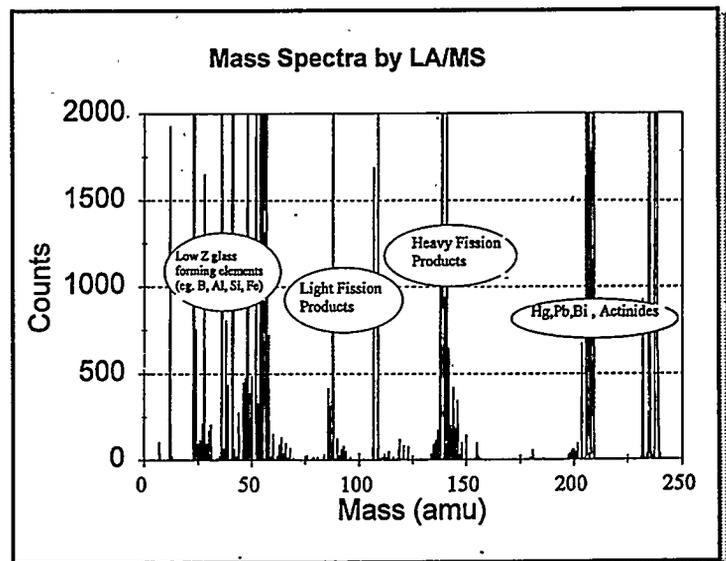


Figure 1.1-1. This graph illustrates sample spectra by LA/MS.

disassociation of the sample plume particles into atomic species and ionization of atoms take place. The ionized atoms enter the MS and are analyzed to determine the number of atoms at each atomic weight for the sample. The resulting data set or particle count at each mass number provides a direct indication of the elemental and isotopic species and their populations in the target sample.

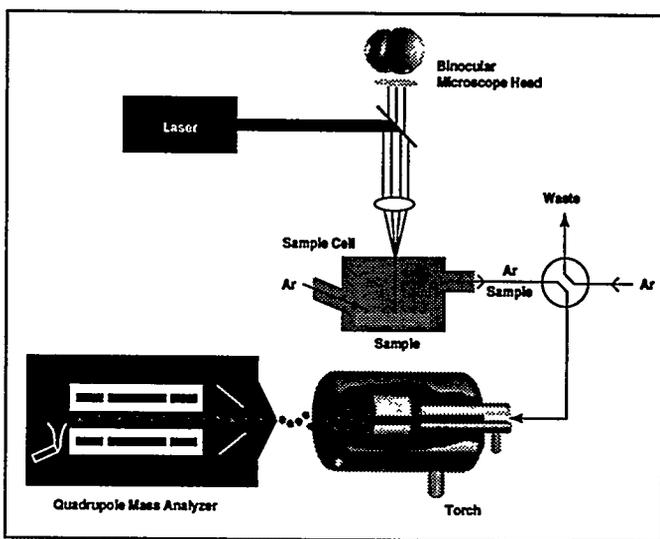


Figure 1.1-2. The LA/MS system includes a pulsed laser for sample ablation.

The LA/MS system is based on commercial instruments and subsystems. The goal of this research is to develop, install, demonstrate, and transfer a hot cell LA/MS system for tank waste characterization. Development this year will address the determination of operating conditions for tank sample analysis and practical performance expectations, development of an integrated hot cell analysis system using commercial equipment, and demonstration of a practical system to meet tank characterization needs.

## BENEFITS

The LA/MS analytical method reduces time and cost for elemental and isotopic analysis on extruded cores; scans cores for sample homogeneity, stratification, and sample selection; and provides data beneficial to characterization, retrieval, pretreatment, and immobilization of tank waste. During operation, samples weighing only nanograms, versus traditional methods that require milligram quantities, are required for complete chemical analysis. The entire characterization process takes approximately one minute. This operation consumes a shorter time period than current methods requiring hours of work. Currently, tank waste samples undergo dissolution/fusion and homogenization processes prior to characterization. These processes can require several days to more than one week. Also, present methods create the potential for unnecessary radiological contamination due to unnecessary sample handling. The LA/MS minimizes this problem because the analysis will be done within a hot cell and an associated fume hood, requiring no sample preparation. The LA/MS system is safer and provides data in a more timely, cost-effective manner. The LA/MS system is planned for deployment in the fourth quarter of FY96.

## **COLLABORATION/TECHNOLOGY TRANSFER**

LA/MS is co-funded by EM-30 and EM-50. The EM-50 development scope includes technical risk reduction, method validation, equipment procurement and fabrication, system cold assembly and testing, and initial hot cell system validation. The EM-30 scope, although considerably shorter, is important for guaranteeing system deployment. This scope includes hot cell system hardware engineering, hot cell facility preparation, and hot cell system assembly and testing.

## **ACCOMPLISHMENTS**

- Hot cell system hardware engineering was initiated during the first quarter of FY96.
- Computer algorithms are being developed for automated data acquisition and analysis.
- Tests on simulated and real samples are running on parallel paths to validate system deployment and transfer.

## **TTP INFORMATION**

Advance Hot Cell Analytical Technology - Laser Ablation/Mass Spectroscopy technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36WT21, "PNNL Characterization/AHCAT-Laser Ablation/Mass Spectroscopy"

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Alexander, M.L., M.R. Smith, D.W. Koppenaal, and J.S. Hartman. "Laser Ablation ICP/MS Analysis of Low Level Hanford Tank Waste and Simulants: Optimizing Experimental Parameters," Rocky Mountain Conference on Analytical Chemistry (1995).

Figg, D., M. Kahar, N. Nogar, M.R. Smith, and M.L. Alexander. "Picosecond Laser Ablation Studies using ICP/MS and Particle Size Measurement," Thirty-fifth ORNL-DOE Conference on Analytical Chemistry in Energy Technology (1994).

## 1.2

# NEAR INFRARED SPECTROSCOPY

### TECHNOLOGY NEED

Moisture is one of the key elements influencing the safety status of some of Hanford's HLW tanks. Ferrocyanides were added to tank wastes to increase the available storage space when production outstripped the ability to provide adequate storage space. Organics from some of the extraction processes used at Hanford ended up in tanks because of inefficient reagent recovery processes. Moisture provides a thermal buffer for the prevention of ignition and propagation of thermal reactions in wastes containing ferrocyanides or organics. Insufficient moisture level raises the possibility of explosion. The conditions for a thermal event are reduced by the presence of water in the wastes. A method is needed to measure and quantify tank waste water concentrations.

### TECHNOLOGY DESCRIPTION

The Near Infrared (NIR) Spectroscopy characterization tool is being developed for screening tank waste samples for determination and quantification of moisture content. The objective of this project is to provide a hot cell NIR probe for making moisture measurements of tank waste cores and grab samples. NIR spectroscopy is a well-established technology with many commercially available components and modules.

The concentration of water in waste samples is determined by measuring the optical absorption caused by the water. The vibrational states of water produce a strong infrared absorption that is normally an interferant in the use of infrared techniques with materials containing water. The high strength of this infrared absorption produces strong overtone bands in the near infrared optical region which are compatible with conventional fiber optic and optical components. Radiation-hardened fiber optic probes allow remote sensing in the radioactive and caustic environments of the Hanford underground storage tanks.

Moisture is extracted from the near infrared spectra to apply Partial Least Squares (PLS) numerical analysis techniques. A model is first generated with standard samples having known concentrations of water. Spectra from unknown samples are then processed by the PLS calibration model to produce a water content value.

The spectrometer system uses both the 1.4 and 1.9 micron water absorption overtones. Currently, a conventional laboratory Fourier Transform Infrared (FTIR) system from BioRad Corporation is being used to record spectra and to provide spectral/PLS model processing. This system will be replaced by a

system (Polytec PI X-DAP) that is more user friendly and will simplify and reduce operator interfacing. This system uses an imaging spectrometer and a Incas (indium-gallium arsenide) detector array to cover these water overtone bands.

The moisture detection probe is shown in Figure 1.2-1. The probe was purchased through Axiom Corporation. The probe's outer housing, indicated by the large outer circle, is stainless steel with a sapphire window attached to the end of the housing. The fiber cable furnished with this probe was custom-designed and consists of a random distribution of 40 illuminating and 40 detecting fibers mounted in an SMA-095 connector housing. The fibers are 100 microns in diameter.

The focus this fiscal year is to develop a process to acquire and determine moisture content from the data sets that is both cost-effective and time-efficient. This involves establishing a firm baseline approach for the mathematical model, finalizing any operating safety issues, and training operators.

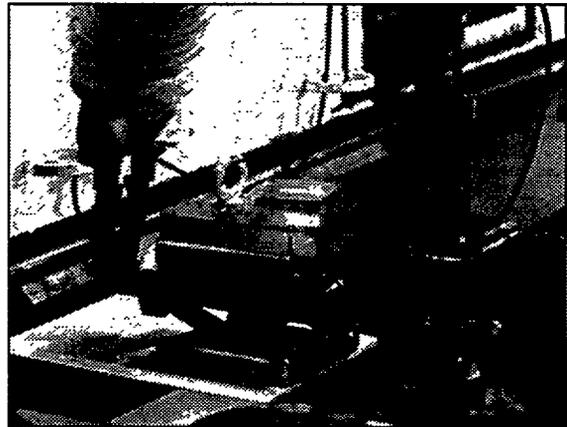


Figure 1.2-1. The near infrared probe outer housing is stainless steel.

## **BENEFITS**

The current thermogravimetric analysis (TGA) method, based on loss of weight, uses a very small sample volume affected by particle size and sample morphology. In addition, during the handling time prior to determining moisture content using TGA, the sub-samples can lose or gain moisture from operator manipulation and exposure to different surrounding environments. The NIR moisture probe does not require sample preparation. With an NIR hot cell moisture probe, moisture data are obtained immediately after core extrusion and from a more representative waste sample. Also, the probe generates moisture profiles along the length of an extruded core, and moisture concentration as a function of core thickness. A hot cell NIR moisture probe will augment the flow of tank materials through the hot cell by reducing the time needed to make a moisture measurement and reducing the error induced by current handling and sampling limitations.

## **COLLABORATION/TECHNOLOGY TRANSFER**

NIR technology is reasonably well established. Three companies have applied for a license to produce the probe. An agreement was signed with EM-30, Tank

Waste Remediation System Division, to develop this technology under the "fast track" accelerated strategy. A work plan was initially developed that described the activities, milestones, deliverables, and task assignments to complete the FY95 "fast track" activities. A "fast track" team was formed with Westinghouse Hanford Company (WHC) technical staff members from WHC's Remote Systems and Sensor Applications and Process Analytical Chemistry groups to coordinate these activities.

### ACCOMPLISHMENTS

- NIR Spectroscopy was demonstrated on both simulants and real tank wastes in FY95.
- Installation of the NIR moisture probe into a hot cell facility (see Figure 1.2-2) was completed in January 1996.
- Hot Cell data collection with real sample cores is currently taking place for comparison with TFA methods.

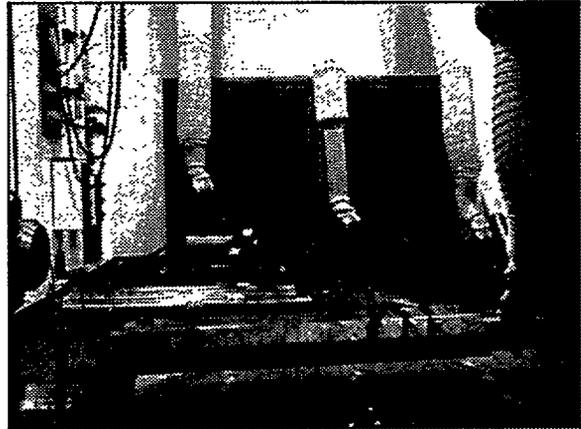


Figure 1.2-2. The NIR moisture probe was installed in a hot cell facility.

### TTP INFORMATION

Near Infrared Spectroscopy technology development activities are funded under the following technical task plan (TTP):

TTP No. RL46WT21, "WHC Characterization"

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## 1.3

# RAMAN PROBE/CONE PENETROMETER

### TECHNOLOGY NEED

The need for chemical characterization of the tank wastes is driven by both safety and operational considerations. Safety drivers include the monitoring of organic chemicals and oxidizers to address flammability and energetics, nitrate and nitrite levels to address corrosion concerns, plutonium levels to address criticality prevention considerations, and detection of organic and inorganic species to identify chemical incompatibility hazards associated with ferrocyanides, nitrates, sulfates, carbonates, phosphates, and other oxyanions. Operational concerns include the monitoring of phosphate levels driven by the potential formation of sodium phosphate crystals, thereby increasing the viscosity of the waste by formation of a gelatinous matrix which will reduce the ability of pumps to transfer and retrieve waste.

Current techniques of tank waste analysis involve the removal of core samples from tanks, followed by costly and time consuming wet analytical laboratory testing. Savings in both cost and time could be realized in techniques that involve in situ probes for direct analysis of tank materials.

### TECHNOLOGY DESCRIPTION

Raman spectroscopy is a powerful tool for the characterization of unknown chemical constituents by probing the vibrational energies of the molecules. A laser-based technique, Raman spectroscopy can use readily available laser light sources in the visible and near infrared to interrogate samples. These regions of the light spectrum, in particular the near infrared, are also efficiently transmitted over long distances by fiber optics, making Raman an essential tool in remote access spectroscopy. Being a vibrational technique, Raman spectroscopy is a nonspecific technique that can be used to identify and measure a large suite of inorganic and organic chemical species. Single point, fiber optic probes, which interrogate a sample one point at a time, have been highly successful in identifying key tank components such as nitrate, nitrite, and ferrocyanide in simulated and archived tank samples. Raman spectroscopy was identified by an independent panel during the FY94 tank characterization peer review as the spectroscopic technique most qualified for use in the characterization of tank wastes.

The in-tank cone penetrometer (CPT) provides a path for in situ tank waste characterization. A Raman probe interfaced within the CPT housing brings interrogative methods to the tank waste matrix in its native environment, providing faster, safer, and more cost-effective tank characterization both in

terms of time and effort. Currently, a single core extrusion costs nearly \$1 million. Preparation and planning for sample extraction can take up to three months.

The cone penetrometer system (see Figure 1.3-1) consists of a series of 3-foot long steel hardened hollow rods that encapsulate the Raman probe or any other analysis system capable of penetrating to a depth over 100 feet. The probe will be pushed into the sample surface and interior with an applied force supplied by the overhead containment system. The sensors built into the cone penetrometer provide measurements of penetrometer tip pressure, sleeve friction, pore pressure, electrical resistivity, tip temperature, penetration depth, penetrometer inclination, and magnetic bottom detection. These sensors provide characterization of the physical properties of the tank wastes that impact operational considerations for tank waste retrieval. However, the current penetrometer platform provides no characterization of the tank wastes, a major safety and operational concern.

The cone penetrometer under development is currently available for incorporation with the Raman probe. A prototype Raman probe was delivered to Applied Research Associates (ARA) and WHC in January 1996 for validation testing with incorporation of the cone penetrometer and additional systems. Safety and operational testing for system deployment in FY96 are also being conducted. Radiation and chemical testing of the fiber optic Raman probe and the cone penetrometer Raman probe housing will be performed using a gamma radiation pit with a radiation rate of 600 Rad/hour. The purpose of these tests is to determine the integrity of the cone penetrometer Raman probe housing stability. The degree of chemical attack over time will also be determined.

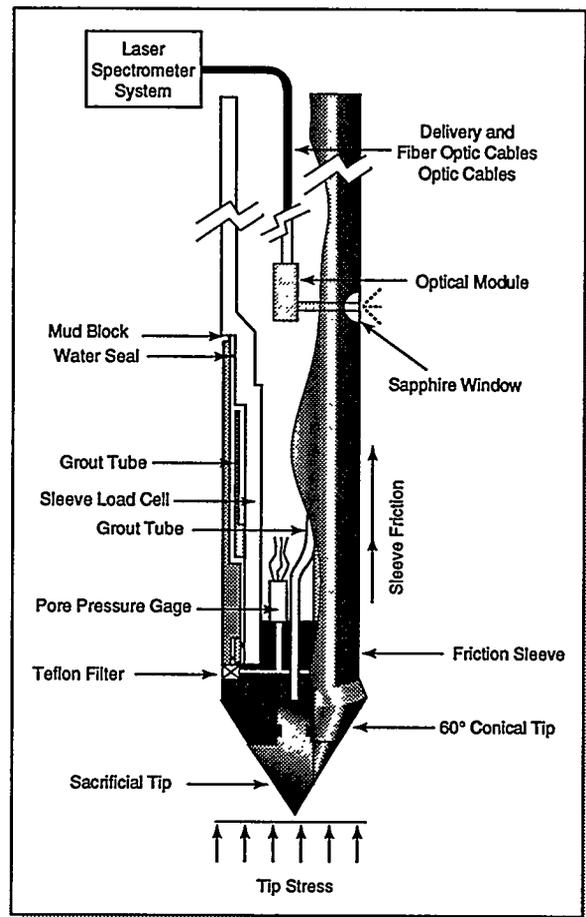


Figure 1.3-1. Hollow steel rods encapsulate the cone penetrometer probe.

## BENEFITS

A cone penetrometer deployed Raman probe offers the great advantage of in situ chemical analysis and depth profiling of tank wastes without the prior removal of waste materials. This technique reduces the risk of contamination caused by sample transportation and handling, minimizes exposure of personnel to radioactive contaminants, significantly reduces or eliminates sample generation, and provides significant cost savings. The cone penetrometer equipped with a Raman probe provides a method of depth profiling of the tank waste in a few hours from surface to bottom. This combination provides in situ characterization of the tank components, addressing safety and operational considerations during tank waste retrieval and remediation operations.

## COLLABORATION/TECHNOLOGY TRANSFER

WHC has contracted ARA to construct and deploy a 35-ton cone penetrometer and an associated instrument and control trailer (see Figure 1.3-2) for use in characterizing the properties of the slurries, sludges, and saltcakes of the Hanford tank farms. Lawrence Livermore National Laboratory (LLNL) is providing a fiber optic remote Raman chemical sensor system for incorporation and deployment in the ARA in-tank cone penetrometer to address these chemical safety and operational needs. Physical Optics Corporation was contracted to develop a neural network signal extraction and enhancement system. The system is a software analysis package for data reduction and manipulation. A first version of the software is scheduled to be delivered to LLNL in the third quarter of FY96.

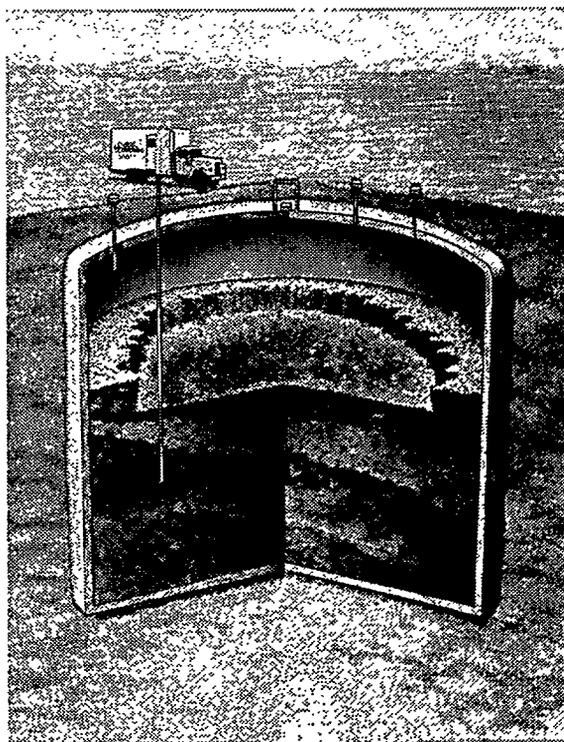


Figure 1.3-2. The cone penetrometer will be deployed with a control trailer.

GRX-96-0125

## ACCOMPLISHMENTS

- Successfully finished the cone penetrometer push test
- Constructed the Raman probe housing for incorporation with the cone penetrometer
- Fabricated the sapphire probe window with braze
- Tested most components for integration with the cone penetrometer

## TTP INFORMATION

Raman Probe/Cone Penetrometer technology development activities are funded under the following technical task plan (TTP):

TTP No. SF26WT21, "LLNL Characterization: In Situ Cone Penetrometer Raman Probe"

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# 1.4

## ELECTRICAL RESISTANCE TOMOGRAPHY/ CONE PENETROMETER TANK LEAK DETECTION AND MONITORING

### TECHNOLOGY NEED

Single-shell and double-shell waste tank design is common across the DOE complex. The single-shell tanks present potential environmental hazards because only a single barrier contains the liquids and any breach in the barrier will cause contaminant spillage. A sluicing method being considered to retrieve the waste requires thousands of gallons of water, raising the possibility of HLW leakage into the surrounding environment. In other tanks, water is added to prevent the waste matrix from drying and provides a deterrent from possible ignition due to flammable gases. There is a need to develop instrumentation to determine the location of a leak, the amounts of materials that were exposed, and the quantity of the contaminant material.

### TECHNOLOGY DESCRIPTION

Electrical Resistance Tomography (ERT) is a leak detection technique in the family of methods that uses electricity and electrical properties. Tank contents vary but typically the liquids are highly saline and therefore electrically conductive. ERT is a geophysical imaging technique that maps liquids migrating through the soil by measuring the resistivity or voltage fluctuation caused by a migrating plume (see Figure 1.4-1). By introducing electrodes into the soil and measuring voltage changes that occur between electrodes surrounding a suspected leak location, information about the location, volume of the leak, direction, and rates of movement of the fluid can be determined.

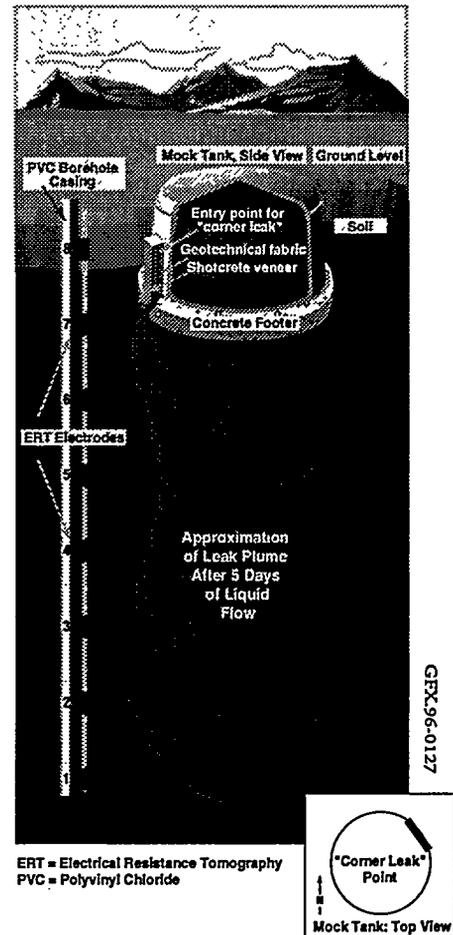


Figure 1.4-1. ERT/CPT leak detection electrodes measure voltage changes around a suspected leak.

This project has three technology development goals. The first is development, demonstration, and technology transfer of ERT for monitoring tank leaks. If successful, the second goal is a full-scale demonstration on an underground storage tank during sluicing operations which will be scheduled in FY97. The third goal is to extend the data processing algorithms to three dimensions, for a three-dimensional map of the leak plume. In addition, the task includes preparation of a study to investigate the feasibility of using such a deployment technique and leak detection/monitoring (LDM) tool in an actual tank farm, with consideration of various operational, logistical, physical, political, safety, and other topics.

## **BENEFITS**

There are two methods of detecting leakage from tanks: monitoring the liquid level of waste in the tanks and monitoring the soil under the tanks for leaks. Liquid level sensors can signal a leak but are of limited sensitivity and provide no information about the location of the leak or the distribution of the resulting plume. The heterogeneous finger-like structure of liquid transport through soil would require hundreds of sensors around and underneath a tank to ensure reliable detection of chemical contaminant leaks, and would be costly.

Based upon previous experience, the Cone Penetrometer (CPT) technique has been shown to have the capability and potential to deploy ERT electrodes to depths greater than 50 feet beneath the soil surface, the region of interest for single-shell tank (SST) leakage monitoring and detection. The CPT, capable of placing a single, small diameter probe into the ground by "pushing" the unit to the required depth, will be developed and tested as a deployment tool for ERT. Drilling boreholes for ERT to achieve the same degree of deployment as ERT-CPT would be more expensive and would pose additional operational and technical problems, especially when attempted in an actual SST tank farm. The use of CPT could save substantial funds and overcome most of the tank farm technical deployment problems.

## **COLLABORATION/TECHNOLOGY TRANSFER**

The task involves the deployment of prototypical CPT-deployable ERT electrodes (see Figure 1.4-2), and testing and verification of the ERT data-gathering capability from such electrodes by comparison to previous ERT leak test data. EM-50 will provide funding to ARA to develop a prototype CPT probe(s) configuration that incorporates ERT electrodes, and emplaces an electrode array to a depth between 50 to 150 feet into Hanford soil. An additional contract will be provided to LLNL to provide technical assistance regarding ERT during the CPT well development process, to verify that the CPT-deployed ERT electrodes function as previously demonstrated, and to participate during actual field testing of the prototype electrodes at Hanford.

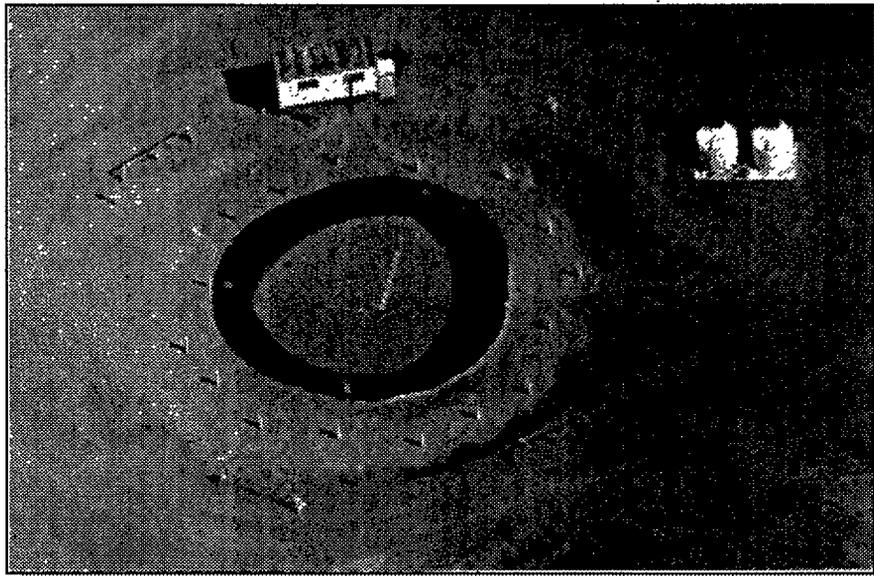


Figure 1.4-2. A typical ERT leak detection system will be installed.

### ACCOMPLISHMENTS

- Two field experiments were performed to evaluate the performance.
- Two- and three-dimensional tomographs and two-dimensional current maps were calculated from performance experiments.
- Field results indicated the plume associated with the release could be reliable for leak monitoring and detection.

### TTP INFORMATION

ERT/CPT Tank Leak Detection and Monitoring technology development activities are funded under the following technical task plan (TTP):

TTP No. RL46WT21, "WHC Characterization"

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## 2.0

# WASTE RETRIEVAL AND TANK CLOSURE OVERVIEW

Underground tanks throughout the DOE complex in Hanford, Savannah River, Oak Ridge, and Idaho have stored a diverse accumulation of wastes during the past fifty years of weapons and fuel production. If these tanks were entrapped in a manner that would preclude the escape into the environment for hundreds of years, there would be no reason to disturb them. However, a number of the storage tanks are approaching the end of their design life. At the four sites, 90 tanks have either leaked or are assumed to have leaked waste into the soil and sediments near the tanks.

Recently, dewatering processes have removed much of the free liquid. The tanks now contain wastes ranging in consistency from remaining supernate and soft sludges to concrete-like saltcake. Tanks also contain miscellaneous foreign objects such as Portland cement, measuring tapes, samarium balls, and in-tank hardware such as piping. Unlimited sluicing, adding large quantities of water to suspend solids, is the baseline method for sludge removal from tanks. This process is not capable of retrieving all of the material from tanks. Its use has been questioned by stakeholders due to the existing and potential leaks of hazardous and radioactive liquids from corroded and deteriorated tanks into nearby soils and groundwater. Besides dealing with aging tanks and difficult wastes, retrieval also faces the problem of the tank design itself. Retrieval tools must be able to enter the tanks, which are under an average of 10 feet of soil, through small openings called risers in the tops of the tanks. The Retrieval and Tank Closure functional area of the TFA is developing technologies and tools for this purpose.

Retrieval and Tank Closure process development will provide tools and process alternative enhancements to mixing and mobilizing bulk waste as well as dislodging and conveying heels. Heel removal is linked to tank closure. The working tools and removal devices being developed include suction devices, rubblizing devices, water and air jets, waste conditioning devices, grit blasting devices, transport and conveyance devices, cutting and extraction tools, monitoring devices, and various mechanical devices for recovery or repair of waste dislodging and conveyance tools. For some retrieval operations, small amounts of water may need to be added to facilitate waste dislodging and removal. Systems are being optimized to minimize the amount of water added to tanks, and to position the conveyance equipment deployed with the dislodging equipment to remove solid waste and free liquid as promptly as possible. Dislodging and conveyance tools will ultimately be deployed as end effectors on a remotely operated, articulated arm such as the Light Duty Utility Arm (LDUA) or Houdini Vehicle being developed by the Office of Science and Technology Robotics Program. They will need to be capable of performing in

a radiation environment of up to 10,000 rad/h and withstanding an accumulated dose of  $10^6$  rad.

Retrieval and Closure activities also aim towards identifying existing processes and technologies that can be used to reduce cost, improve efficiency, and reduce risk. Mixer pumps, enhanced sluicing, pulsed air mixer, borehole mining, acquired commercial technology for retrieval, and density gradient mixers are the products of this effort.

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## 2.1

# LIGHT DUTY UTILITY ARM SYSTEM

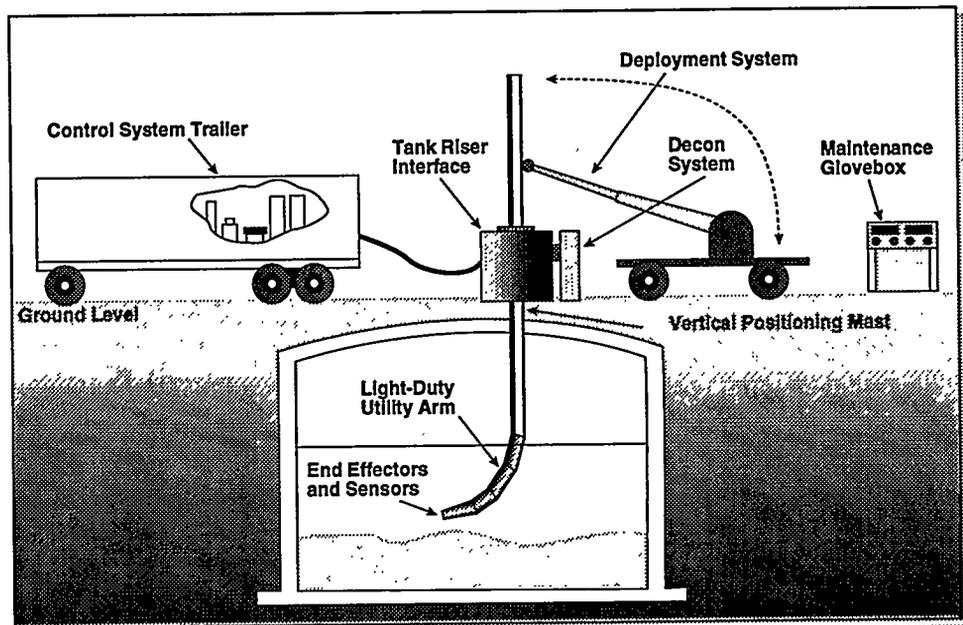
### TECHNOLOGY NEED

Remediation of hundreds of underground storage tanks containing millions of gallons of hazardous, radioactive waste poses many challenges due to the hazardous environments, access limitations, and lack of available technologies to perform many tasks required in the cleanup process. In large underground storage tanks that have been in operation for several decades, the areas directly below the access risers are often disturbed or contain a significant amount of discarded debris. Therefore, evaluation of tank waste characteristics by measurements taken at these locations may not be representative of the properties of the waste in other areas of the tanks.

To monitor current conditions and plan for tank remediation, more information on the tank conditions and their contents is required. Current methods used at DOE tank sites are limited to positioning sensors, instruments, and devices to locations directly below access penetrations. These systems can only deploy one type of sensor, requiring multiple systems to perform more than one function in the tank. The capability to perform close-up examinations of the tank walls is not currently available, and inspection of single-shell tanks is limited to videos or still photography taken from positions directly below access risers. Visual examinations using current photography and video systems provide useful but limited information. A robotic arm is an effective way to address these problems and needs.

### TECHNOLOGY DESCRIPTION

The Light Duty Utility Arm (LDUA) system (see Figure 2.1-1) provides a mobile multiaxial positioning system that will access the underground storage tanks through existing 12 inches diameter riser penetrations in the tank domes to perform tank structural integrity assessments and to examine characteristics and properties of the waste. Other ancillary system equipment will be deployed through existing 4 inches diameter risers. The system provides the capability to deploy remotely operated end effectors at multiple elevations and positions within the tank using a robotic manipulator arm mounted on a telescoping mast. The LDUA system is functionally divided into major equipment subsystems and additional ancillary and support equipment. These subsystems include: arm and deployment, tank riser interface and confinement (TRIC), operations control center, end effectors, and various utilities and interface equipment that support multiple subsystems.



GFX-96-0187

Figure 2.1-1. The LDUA system uses existing penetrations in tank domes.

The LDUA will be capable of being operated in either remote or automated modes. The manipulator arm will provide a radial reach of at least 13.5 feet from the tank riser centerline. The kinematic design, based on seven degrees of freedom, results in a highly dexterous positioning capability. The arm will provide a lifting capacity of at least 50 pounds at maximum extension, with the capability to lift end effectors up to 75 pounds with some compromise to the system accuracy parameters. The deployment mast will provide extension to at least 62.5 feet to access the full tank depth.

## BENEFITS

The LDUA system is targeted at delivering a remotely operated, mobile deployment system which can access tanks through existing access ports, or risers, to perform multiple tasks. The LDUA system provides the first opportunity to deploy sensors and other devices in locations away from directly below the access risers. This capability is particularly important in analysis of the waste materials in the tank. The system will be capable of performing tasks such as assessing tank structural conditions, characterizing the waste materials, and performing small-scale retrieval operations. The LDUA System will also allow multiple examination tools to be deployed during a single examination campaign, significantly reducing costs of operations.

## **COLLABORATION/TECHNOLOGY TRANSFER**

The LDUA system is actually built around the robotic arm which is the centerpiece component of the system. This arm and deployment system (including mobile platform, interface to the TRIC, telescoping vertical positioning mast and housing, and deployment vehicle) are all being developed by commercial companies with SPAR Aerospace as the prime developer and supplier of the articulated arm. Of the original arm ordered and the options for four additional arms, one was ordered by EM-50 and three additional have been ordered by the customers. In addition to the arm itself and the deployment subsystem, the program is developing, in cooperation with National Instruments, the computer interface for the LDUA system.

The LDUA System is currently planned for in-tank demonstrations conducted in partnership with EM-30 and EM-40 users at the Hanford (EM-30), Idaho National Engineering Laboratory (INEL, EM-30), and Oak Ridge National Laboratory (ORNL, EM-40) sites in FY96 and FY97. During FY96, detail design and specification for the ORNL end effector will be completed and procurement/fabrication initiated. Procurement of the INEL end effector is not anticipated to begin until FY97.

## **ACCOMPLISHMENTS**

An LDUA was delivered to the cold test facility at the Hanford site to test and qualify the system equipment before hot operations in underground storage tanks at Hanford and INEL.

Other technology development activities related to LDUA are:

- LDUA Supervisory Control & Data Acquisition to advance control technologies
- Mini-Lab end effector to perform in situ waste analysis, reducing the need for samples to be removed from the tank
- Remote Viewing Technology to improve the quality of operation, reduce the potential for personnel exposure and provide necessary components for remote operations
- Topographical Mapping System as a sensing technology for characterization and remediation activities

## TTP INFORMATION

LDUA System technology development activities are funded under the following technical task plans (TTPs):

TTP No. RL46WT51, "Subtask 1 - LDUA Systems"

TTP No. OR16WT51, "Subtask 1 - Topographical Mapping"

TTP No. ID76WT51, "Subtask 7 - INEL LDUA Minilab"

TTP No. SR16WT51, "Task 1 - LDUA Remote Viewing Systems"

TTP No. AL26WT51, "Subtask 1 - LDUA Supervisory Control & Data Acquisition Systems"

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## 2.2

# WASTE RETRIEVAL AND TANK CLOSURE DEMONSTRATION

### TECHNOLOGY NEED

Currently, decisions regarding necessary retrieval technologies, retrieval efficiencies, retrieval durations, and costs are highly uncertain because no basis has been established regarding how clean a tank must become before it can be closed. Likewise, the absence of tank closure criteria makes it difficult to determine initial monitoring requirements for a closed tank. Demonstrating that tank closure criteria can be developed and implemented will provide substantial benefit to DOE.

To demonstrate that tank closure criteria can be developed and applied, Tank 19F at Savannah River has been selected. The process for closure of this tank has broad applicability to closure of other tanks at Savannah River, Hanford, Idaho, West Valley, and Oak Ridge. As the result of past operations, 1 million gallons of salt were retrieved from Tank 19F and a 30,000 gallon heel that the existing agitation pumps cannot remove is left on the tank bottom. Another important need to be addressed with the proposed work is the evaluation of costs and benefits which will help in making determinations of the cost-benefit tradeoffs between various combinations of waste retrieval operations, treatment operations, and closure configurations. Current technology for salt removal at Savannah River requires construction of large steel support structures over each tank upon which multiple agitation pumps are mounted, resulting in high construction and operating costs. Alternative technologies that offer lower installation and operating costs are needed.

### TECHNOLOGY DESCRIPTION

Technologies are to be developed to address both salt and heel removal processes. The salt removal demonstration will be performed on an HLW tank and will be used to supply feed to the Defense Waste Processing Facility feed preparation process. The demonstration will evaluate two technologies, a density gradient salt removal process conducted in two phases, and a single, existing agitation pump for salt removal. The task will also evaluate the need for other hydraulic salt removal processes, including the use of the water jet for heel removal. If justified, and after consultation with the Tank Focus Area (TFA), this task will demonstrate a third salt removal technique for comparison to the other two and the current baseline process.

The heel removal demonstration will show the effectiveness of a water jet to break up and later remove the solid deposits (salt, sludge, zeolite) in Tank 19F.

The demonstration will utilize the support structures and service facilities that were previously installed on the tank when 1 million gallons of salt were retrieved. The installation of the remaining waste removal facilities (agitation pumps and tank washing facilities) also could be used to complete the demonstration by removing the heel material and/or cesium activity contained in the heel from the tank. The key performance factors to be demonstrated are the pressures and flowrates of dissolution material required to break up the heel; the volume and radioactivity remaining in the tank after the demonstration; subsequent waste retrieval activities; and the time required.

### **BENEFITS**

A collaborative effort between Savannah River's EM-30 Waste Management Program and the EM-50 Tank Focus Area will demonstrate that 1) portions of the residual waste within Tank 19F can be removed, 2) closure criteria for the tank can be developed and implemented, and 3) salt removal can be accomplished at a much reduced cost from the current baseline.

### **COLLABORATION/TECHNOLOGY TRANSFER**

The proposed technology will be transferred to Savannah River's EM-30 High-Level Waste Management Division. The task is part of a collaborative retrieval and closure demonstration that is being jointly funded by the Tank Focus Area and Savannah River's operational budget. An industrial partner is currently not required for implementation of this technology by Savannah River Waste Management personnel. However, there is a significant opportunity to obtain private industry involvement in the development and supply of equipment that will meet the technical requirements for heel removal and/or salt dissolution. These inputs are being obtained through the procurement process for anticipated waste retrieval/heel removal equipment. The demonstrated technology and data will be transferred to other DOE sites such as Hanford.

### **ACCOMPLISHMENTS**

- Designated task program manager and supporting team members at Savannah River Site (SRS)
- Selected Tank 41H, salt removal, and Tank 19F, heel removal and closure to perform demonstrations
- Submitted Program Plan to DOE-HQ
- Issued Functions and Requirements Document for Tank 41H

- Developed and implemented Density Gradient Salt Removal for HLW operations for demonstration
- Reviewed Heel removal data with water jet at West Valley

### **TTP INFORMATION**

Waste Retrieval and Tank Closure Demonstration technology development activities are funded under the following technical task plan (TTP):

TTP No. SR16WT51, "Subtask 1 - Waste Retrieval and Tank Closure Demonstration"

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Waters, R.D., D.A. Bougai, and P.I. Pohl. "Screening-Level Performance Evaluation for RCRA Toxic Metal Disposal in DOE Low-Level Radioactive Waste Disposal Facilities," Draft Report (1995).

## 2.3 RETRIEVAL PROCESS DEVELOPMENT

### TECHNOLOGY NEED

Across the DOE complex, each site has distinct differences in tank construction, tank materials, amount of in-tank hardware, waste forms, tank integrity, as well as a multitude of other differences. The retrieval of waste from underground storage tanks is the problem for Retrieval Process Development (RPD).

A related problem that RPD is examining is the current lack of a retrieval decision support tool for the end users. As development activities move forward toward collection of retrieval performance and cost data, it has become very evident that the various sites across the complex need to have a decision tool to assist end users with respect to tank retrieval and closure. Tank closure is intimately tied to retrieval, and the sensitivity of closure criteria to tank retrieval is expected to be very large.

### TECHNOLOGY DESCRIPTION

The overall purpose of RPD is to continue to lead the TFA efforts in the basic understanding and development of retrieval processes in which waste is mobilized sufficiently to be transferred out of tanks in a cost-effective and safe manner. From that basic understanding, data are provided to end users to assist them in the retrieval decision-making process.

RPD activities for FY96 address the issues at ORNL, INEL, Hanford and SRS. At ORNL, there are Gunite tanks in the North and South tank farms ranging from 25 feet to 50 feet in diameter. There are two tank systems at INEL that are problems for RPD. The first is the stainless steel underground storage tanks that are lined on the sides and bottom with cooling coils. The cooling coils cannot be removed prior to retrieval, and since they are roughly three to six inches from the bottom, techniques for cleaning the coils and underneath the coils are required. The problem at Hanford is the waste in the 177 underground storage tanks, both single and double-shell. The problem for the 149 single-shell tanks is the retrieval of difficult saltcake and sludges with various amounts and types of intank hardware and debris. At Savannah River, there are 51 underground storage tanks. The problem is very similar to the Hanford underground storage tanks, in that vast quantities of saltcake and sludge exist that need to be removed effectively and efficiently. Furthermore, zeolite from ion exchange processes is in several of the SRS tanks.

The focus of these activities is to transfer the retrieval processes being developed towards field deployable systems that have been identified by end

users across the DOE complex. The retrieval process includes system deployment, dislodging, mixing, sluicing, and conveyance in general, and the process is not specific to various deployment systems. The RPD tasks include support of: 1) retrieval end effector deployment for the ORNL Gunite And Associated Tanks - Treatability Study (GAAT-TS), 2) retrieval end effector deployment for the INEL Heel Removal Project, 3) the SRS Retrieval and Closure Demonstration, 4) technical assistance to and integration with the Hanford Acquired Commercial Technology for Retrieval (ACTR) program, 5) support for the retrieval and closure portions of INEL V-Tank remediation, 6) simulant development, 7) sensor and instrumentation development for retrieval process evaluation, 8) integrated testing, and 9) system leadership/program management.

## **BENEFITS**

It is also the purpose of these activities to begin to develop a retrieval decision analysis tool that can be employed across the complex. The decision tool will incorporate technical data for performance, as well as expected performance, programmatic risks of various technologies, life cycle cost, and closure. The tool will help site end users begin to understand the relationship and sensitivities between retrieval and closure aspects of tank remediation.

## **COLLABORATION/TECHNOLOGY TRANSFER**

RPD activities support the GAAT-TS at ORNL for the purpose of providing confined sluicing end effector technology that will be deployed by the Modified LDUA in FY97. The Gunite tanks in both the North and the South Tank Farms at ORNL contain liquid supernate and sludge. Initial efforts will lead to the retrieval of wastes in Tanks W3 and W4 in FY97. The RPD effort includes support of design reviews, completing prototype testing, providing the detailed design of the confined sluicing end effector, cold test planning, and data requirements and evaluation for both cold testing and hot deployment.

The Heel Removal Demonstration of the INEL stainless steel tanks with cooling coils is expected to begin in FY98. The RPD FY96 INEL effort includes the completion of the Functions and Requirements documentation, prototype testing, and conceptual design efforts leading to equipment acquisition in FY97. The main purpose, similar to that of the Oak Ridge task, is to bring the confined sluicing technology to INEL for retrieval demonstration. At INEL, this demonstration will be with the LDUA. The confined sluicing end effector will be integrated with the LDUA system for the heel removal demonstration.

The Retrieval Process Development will assist SRS in a series of retrieval and closure demonstrations over the next several fiscal years. There are currently three retrieval demonstrations and one closure demonstration planned.

Technical assistance and expertise will be provided to the EM-30 Hanford ACTR program for technical evaluation of the potential application and deployment of existing technology toward retrieval as well as to integrate information from ACTR to the DOE complex. The main purpose for RPD involvement in the Hanford EM-30 ACTR program is to work with ACTR in the demonstration, evaluation, and integration phases of industry retrieval demonstrations.

### ACCOMPLISHMENTS

- A new end effector development activity was started to assess the feasibility of deploying a confined sluicing end effector into the INEL and ORNL tanks to perform waste heel removal.

### TTP INFORMATION

Retrieval Process Development technology activities are funded under the following technical task plan (TTP):

TTP No. RL36WT51, "Subtask 1 - Retrieval Process Development"

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Rinker, M.W., B.K. Hatchel, and O. D. Mullen. "Waste Dislodging and Conveyance Testing Summary and Conclusions to Date," PNL-10095 AD-902 (PNL, WHC) (1994).

## 2.4

# RETRIEVAL ENHANCEMENTS

### TECHNOLOGY NEED

All the existing processes and technologies that could be used as a baseline for tank remediation have not yet been identified. Identifying these processes is one of the TFA's major issues in addressing the tank problems. The overall purpose of Retrieval Enhancements is to continue to lead the TFA's efforts in the basic understanding and development of retrieval processes in which waste is mobilized sufficiently to be transferred out of tanks in a cost-effective and safe manner. From that basic understanding, data are provided to end users to assist them in the retrieval decision-making process. The overall purpose of Retrieval Enhancements is to identify technical enhancements to baseline and/or existing processes that can be used to reduce cost, improve efficiency, and reduce programmatic risk.

### TECHNOLOGY DESCRIPTION

The Retrieval Enhancements activities are organized into the categories of mixer pumps, enhanced sluicing, pulsed air, borehole mining, acquired commercial technology for retrieval, and density gradient.

Mixer pumps are considered to be baseline technologies for both Savannah River and Hanford double-shell tanks for mobilization and mixing of wastes in underground storage tanks. The main purpose of this retrieval enhancement task is to capture advanced mixer pump developments funded by EM-30 at SRS and Hanford.

Past Practice Sluicing is the baseline retrieval technology for the Hanford single-shell underground storage tanks, and is an alternative retrieval technique for the ORNL Gunite tank retrieval. While past practice sluicing may be effective in mobilizing loose sludges, it may or may not be effective in removing hard heels and saltcake without the addition of large quantities of liquid. Therefore, the purpose of the enhanced sluicing activities is to identify various enhancements, ranging from addition of sensors for monitoring the existing process to evaluation of extendible arms with integral nozzles.

Pulsed air is an existing technology that has proven highly effective for the mixing of viscous liquids in tanks. The pulsed air mixing technique utilizes short, discrete pulses of air or inert gas to produce large bubbles near the tank floor. These bubbles rise toward the liquid surface and induce mixing. An array of horizontal, circular plates is positioned just above the tank floor. Pipes connected to each plate supply pulses of gas to the underside of each plate.

Control equipment is used to control the pulse frequency, duration, gas pressure, and plate sequencing to create a well-mixed condition within the tank.

Borehole Mining is also an existing technology that has potential application in sludge and saltcake tanks at Hanford single-shell tanks, INEL V-tanks, ORNL Melton Valley Storage Tanks, and Savannah River tanks. While borehole mining is not a baseline technology, it is an existing technology being identified for use in underground tank remediation efforts. This technology incorporates the deployment of an extendible arm with an embedded nozzle for dislodging, integrated with a water jet pump for conveyance of the waste. This technology was developed for the oil and gas industry and has strong potential to become a baseline technology.

Density Gradient is the baseline for two demonstrations at Savannah River for retrieval of saltcake. This existing technology uses large quantities of water in the saltcake tanks at SRS to dissolve the saltcake for subsequent pumping of the saturated solution. This is accomplished by "flooding" the waste surface with water; as the water migrates through the saltcake, it dissolves the saltcake. A pump that has been placed near the bottom of the tank then pumps the saturated solution out of the tank.

Mixer pump activities in FY96 will focus on providing direct technical support to the EM-30 end users in their mixer pump design efforts leading to vendor selection and determination of the number of mixer pumps for use at Hanford and Savannah River. Enhancements to sluicing include examination of the nozzle designs leading to more effective energy use of the water jet as well as enhancing the ability to deploy, direct, and monitor the water jet performance. Key parameters will include deployment aspects, water pressure, nozzle design, nozzle forces, and water jet distance. Pulsed air will be the subject of additional tests and investigations in FY96, to make it applicable to underground storage tanks. Borehole mining combines existing technology and deployment mechanisms with tank remediation efforts at the INEL V-Tanks. The FY96 work will provide demonstrations of the borehole mining technique for possible FY97 deployment at INEL V-Tanks. The support for ACTR in retrieval enhancements will be in the form of providing existing test beds and simulants as a platform for demonstrating potential technologies.

## **BENEFITS**

Retrieval Enhancements will provide input regarding applicability, alternative techniques and options, cost effectiveness, evaluation of existing designs, and efficiency. It also ensures that both the design information and performance data are available across the DOE complex and ensures consistency of performance data. Implementing various enhancements to past practice sluicing will result in a dramatic increase in performance during retrieval.

## **COLLABORATION/TECHNOLOGY TRANSFER**

Over 75 percent of PNNL's current set of Office of Science and Technology tasks are being performed in collaboration with universities, industry, or other DOE contractors. In the last year alone, over 10 technologies managed through PNNL programs resulted in substantive commercial relationships.

## **ACCOMPLISHMENTS**

- Scaled pulsed air activities were initiated in FY95.

## **TTP INFORMATION**

Retrieval Enhancements technology development activities are funded under the following technical task plan (TTP):

TTP No. RL36WT51, "Subtask 2 - Retrieval Enhancements"

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## 3.0

# PRETREATMENT OVERVIEW

DOE has about 90 million gallons of high- and low-level waste (HLW and LLW) stored in tanks at four primary sites within the DOE complex. Although the total volume of waste is considered HLW, it is neither cost-effective nor practical to treat and dispose of all of the waste to meet the requirements of the HLW repository program and the Nuclear Waste Policy Act.

The current baseline technology systems for waste pretreatment at DOE's tank waste sites are ineffective and expensive. Technology gaps exist. Large volumes of HLW will be generated, while there is limited space in the planned Nuclear Waste Repository for HLW from DOE. Even if adequate space were made available, treatment and disposal of HLW is still very expensive, estimated to be about \$1 million for each canister of vitrified HLW.

Only a small fraction of the waste, by weight, is made up of radionuclides. The bulk of the waste is chemical constituents intermingled with, and sometimes chemically bonded to, the radionuclides. However, the chemicals and radionuclides can be separated into HLW and LLW fractions for easier treatment and disposal. The Pretreatment functional area of the Tank Focus Area (TFA) is developing the chemical processes necessary for separating the HLW and LLW from tank wastes.

Most of the waste stored in tanks was put there as a result of nuclear fuel processing for weapons production. In that process, irradiated fuel and its cladding were first dissolved, uranium and plutonium were recovered as products, and the highly radioactive fission product wastes were concentrated and sent to tanks for long-term storage.

Fuel processing at the Savannah River Site (SRS) did not change substantially from the beginning of operations in about 1955 to the present. While these wastes are fairly uniform, they still require pretreatment to separate the LLW from HLW prior to immobilization. Waste at Idaho National Engineering Laboratory (INEL) is stored at acidic pH in stainless steel tanks. Much of it has already been calcined at high temperature to a dry powder. Tank wastes at Oak Ridge are small in volume (less than 1 million gallons) and radionuclide inventory (0.16 MCi) compared to other sites (33 million gallons and 534 MCi at Savannah River and 55 million gallons and 198 MCi at Hanford).

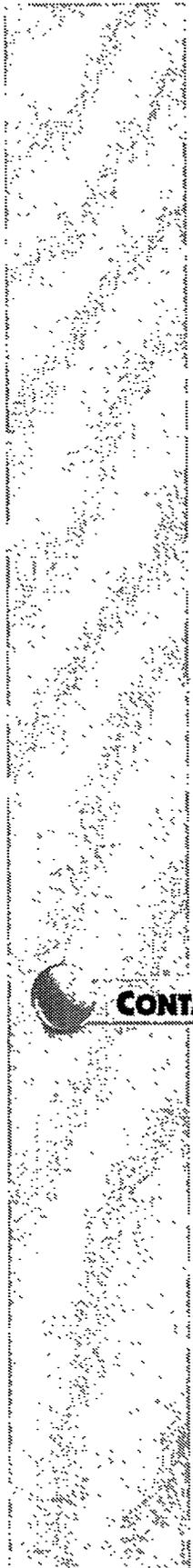
At Hanford, several processes were used over the years (beginning in 1944), each with a different chemical process. This resulted in different waste volumes and compositions. Wastes at Hanford and Savannah River are stored as highly alkaline material so as not to corrode the carbon steel tanks. The process of converting the waste from acid to alkaline resulted in the formation of different physical forms within the waste.

The primary forms of waste in tanks are sludge, saltcake, and liquid. The bulk of the radioactivity is known to be in the sludge which makes it the largest source of HLW. Saltcake is characteristic of the liquid waste with most of the water removed. Saltcake is found primarily in older single-shell tanks at Hanford.

Saltcake and liquid waste contain mostly sodium nitrate and sodium hydroxide salts. They also contain soluble radionuclides such as cesium. Some strontium, technetium, and transuranics are also present in varying concentrations. The radionuclides must be removed, leaving a large portion of waste to be treated and disposed of as LLW and a very small portion that is combined with HLW from sludges for subsequent treatment and disposition.

Waste in tanks has been blended and evaporated to conserve space and has had organic chemicals added during processing. Although sludges contain most of the radionuclides, the amount of HLW glass produced (vitrification is the preferred treatment for HLW) could be very high without pretreatment of the sludges. Pretreatment of the sludges by washing with alkaline solution can remove certain nonradioactive constituents and reduce the volume of HLW. Pretreatment can also remove constituents that could degrade the stability of HLW glass. If the alkaline sludge washing is not effective, some sludges may need to be dissolved in acid and treated by extraction techniques to make a suitable feed to HLW vitrification.

The TFA Pretreatment functional area seeks to demonstrate remediation technologies that address multiple needs across the DOE complex. The primary objectives are to reduce the volume of HLW, reduce hazards associated with treating LLW, and minimize the generation of secondary waste.



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## 3.1

# ENHANCED SLUDGE WASHING

### TECHNOLOGY NEED

The selected treatment for HLW sludges is vitrification and long-term storage in the HLW repository. HLW sludges have varying concentrations of radionuclides as well as a variety of chemical constituents. There are several reasons for this, including the following:

- The wastes came from different chemical processes and are stored in separate tanks.
- Some wastes have undergone further processing (radionuclide removal, evaporation, blending).
- Some wastes are older; radionuclides have decayed and the waste has aged chemically.

Sludge washing can be used to remove various chemical constituents in the waste, allowing them to be treated and disposed of as LLW, which is less expensive and easier to treat and discard.

The concentration of certain chemical constituents such as phosphorus, sulfur, and chromium in sludge can greatly increase the volume of HLW glass produced upon vitrification of the sludge. These components have limited solubility in the molten glass at very low concentrations. Some sludges have high concentrations of aluminum compounds which can also be a controlling factor in determining the volume of HLW glass produced. Aluminum above a threshold concentration in the glass must be balanced with proportional amounts of other glass-forming constituents such as silica. There are estimated to be 25 different types of sludges at Hanford distributed among more than 100 tanks. Samples from 49 tanks would represent approximately 93 percent sludge in Hanford tanks. Testing of Enhanced Sludge Washing (ESW) on all of these samples is needed to determine whether ESW will result in an acceptable volume of HLW glass destined for the repository.

### TECHNOLOGY DESCRIPTION

The combination of caustic leaching and water washing of sludge is known as the ESW process. The purpose of ESW in the waste pretreatment process flowsheets at Savannah River and Hanford is to remove key nonradioactive components from the sludge, leaving the radioactive components, primarily strontium and transuranics, in the solid phase for vitrification in the HLW treatment process. The nonradioactive waste components can be handled

and processed as LLW. ESW is part of the current sludge pretreatment process for Savannah River wastes prior to vitrification in the Defense Waste Processing Facility and is also the baseline process for pretreatment of Hanford sludges prior to HLW vitrification.

ESW is performed after retrieval of waste from storage in tanks. It is currently done in large double-shell tanks (DSTs) at Savannah River and is planned to be performed in-tank at Hanford as well. The alkaline leach and water washing steps are aided by vigorous agitation of the solids using several large mixer pumps. The solids are then allowed to settle, and the liquid is drawn off for processing as LLW. Entrained solids are filtered out and returned to the sludge. The sludge is staged as feed to the HLW vitrification process.

The ESW process itself is rather simple (see Figure 3.1-1). Caustic leaching (typically 3 molar sodium hydroxide) is first used to dissolve certain components of the sludge (e.g., aluminum). The sludge is then washed with "inhibited" water (0.01 molar sodium hydroxide plus 0.01 molar sodium nitrate solution) to remove the interstitial liquid and any remaining soluble solids. The extent of removal of key components (sulfate, phosphate, aluminum, chromium, and radionuclides) is carefully analyzed. These key components will determine the ultimate volume of HLW glass to be disposed of in an HLW repository.

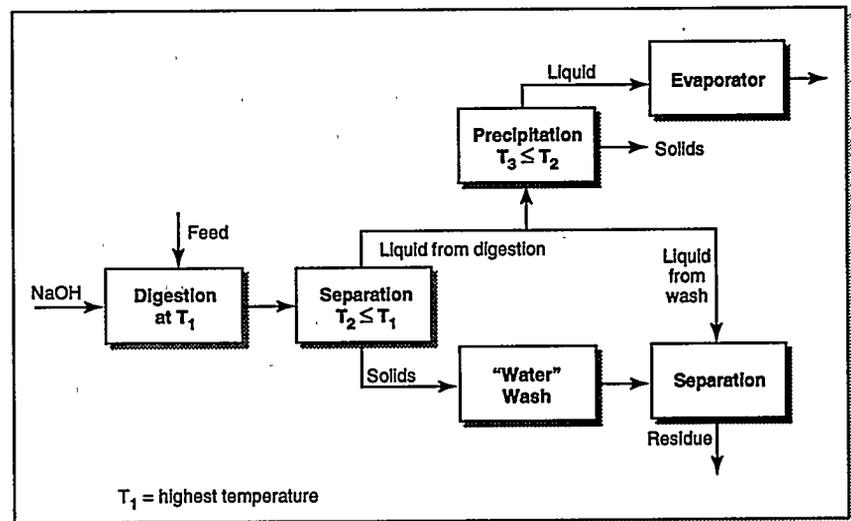


Figure 3.1-1. Enhanced sludge washing is a relatively simple process.

Laboratory-scale testing is being conducted using small samples (about 5 grams) of actual Hanford wastes. Caustic leaching conditions such as concentration and volume of leach solution, temperature, and contact time are being varied to explore optimal conditions for ESW. The technology is currently in the advanced development stage and requires substantial evaluation on a variety of sludge types. The next phases of development will likely be pilot-

scale testing with simulants followed by full scale testing with actual waste just prior to implementation.

### **BENEFITS**

A preliminary cost analysis of ESW for Hanford wastes indicates cost savings of several billion dollars may be realized through implementation of ESW, based upon the reduced volume of HLW glass produced.

### **COLLABORATION/TECHNOLOGY TRANSFER**

This work is coordinated with tasks funded by the Hanford Tank Waste Remediation System (TWRS) and the TFA sludge studies at Pacific Northwest National Laboratory (PNNL) and Oak Ridge. The TWRS work will test sludges from tanks being considered for treatment during Phase I privatization. TWRS will also conduct a full-scale process test using one or more of these sludges by FY97. Other TFA work on alternatives to ESW is being performed at PNNL and Oak Ridge National Laboratory (ORNL). The PNNL work is evaluating ultrasonic processing for improving the caustic leaching performance and oxidizers for removing chromium. The ORNL work is evaluating different caustic leaching process parameters as well as colloid and gel formation. Each is described in detail in a subsequent section of this publication. Testing with actual wastes is necessarily performed in specialized laboratories and hot cells at DOE facilities and typically does not involve outside industry at this stage of development.

### **ACCOMPLISHMENTS**

- This effort has been funded in previous years by Hanford TWRS and performed at both PNNL and Los Alamos National Laboratory (LANL).
- Testing was completed on 18 different sludge samples representing approximately 23 percent of all Hanford sludges.
- Results have been consistent with assumptions regarding aluminum and phosphate removal from sludge.

## TTP INFORMATION

Enhanced Sludge Washing technology development activities are funded under the following technical task plans (TTPs):

TTP No. AL16WT41, "Subtask 1 - Sludge Washing/Alkaline Leach Tests of Actual Hanford Tank Wastes"

TTP No. RL36WT41, "Subtask 3 - Sludge Washing/Alkaline Leach Tests of Actual Hanford Tank Wastes"

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## 3.2

# ENHANCED SLUDGE WASHING ALTERNATIVES FOR HANFORD WASTES AND SLUDGE TREATMENT STUDIES

### TECHNOLOGY NEED

HLW sludges have varying concentrations of radionuclides and a variety of chemical constituents. The concentration of certain key chemicals such as aluminum, phosphorus, sulfur, and chromium can greatly affect the volume of HLW glass produced upon vitrification of the sludge. The combination of caustic leaching and water washing of sludge is known as Enhanced Sludge Washing (ESW) and is designed to maximize removal of the key chemicals. If successful, ESW will result in a reasonable volume of HLW glass to be placed in the repository and will allow processing in existing carbon steel tanks at Hanford and Savannah River.

The efficiency of ESW is not completely understood. Inadequate removal of key sludge components could result in production of an unacceptably large volume of HLW glass. Improvements are needed to increase the separation of key sludge constituents from the HLW.

ESW is planned to be performed batchwise in large double-shell tanks (DSTs) of nominal one million gallon capacity. This will generate substantial volumes of wash solutions which require treatment and disposal as LLW. Settling times for suspended solids may be excessive and the possibility of colloid or gel formation could prohibit large-scale processing. Alternatives are needed that will reduce the amount of chemical addition required and prevent the possibility of colloid formation.

### TECHNOLOGY DESCRIPTION

PNNL is evaluating alternative techniques that can be used in conjunction with alkaline sludge washing to enhance dissolution of key waste components. One specific technique for improving overall sludge dissolution is the use of sonication, or ultrasonic technology. This technology is capable of imparting high energy to chemical systems. Localized hot spots can lead to hundred-fold increases in chemical reactions. This technology is expected to result in more rapid and complete removal of aluminum, sulfate, and phosphate at a lower bulk temperature. Ultrasonic technology is commercially available and is used industrially in cleaning applications. For application to HLW sludges, technology is in the exploratory development stage. This work will demonstrate technical feasibility. Further development would require demonstration of the

technology in an integrated system, identification of specific deployment opportunities, and collaboration with a commercial vendor.

Another alternative being investigated by PNNL is the use of chemical oxidizers to enhance the removal of chromium from certain sludges. This is a continuation of similar work funded in FY95 by the Hanford TWRS. The basis for this technology is that hexavalent chromium, Cr(VI), is soluble in alkaline solution whereas trivalent chromium, Cr(III), is not. Thus treatment with a strong oxidizer such as permanganate is expected to substantially increase the removal of Cr from certain Hanford sludges by oxidizing the insoluble Cr(III) to soluble Cr(VI).

This technology is being developed at the bench scale for application to specific Hanford sludges known to be high in insoluble chromium. The feasibility of permanganate was demonstrated in FY92 and the technology is now at the advanced development stage. Further development (engineering development and demonstration) would be easily incorporated with development of the baseline ESW process since only chemical addition and process conditions would be modified.

Sludge treatment studies are being performed at ORNL to investigate the dissolution behavior of actual tank waste sludges from ORNL Melton Valley Storage Tanks (MVSTs) as well as Hanford tanks. Alkaline sludge washing at conditions other than the Hanford baseline are being evaluated for effectiveness. Alkaline concentrations of up to 6 molar caustic, temperatures up to 100° Celsius, and different volumes of wash solutions are being tested. The behavior of key sludge components including phosphorus, aluminum, and silica is being measured. Conditions under which colloids or gels form are also being observed. Gel formation could effectively prohibit large scale processing using ESW conditions.

Previous work has been carried out at bench scale using simulants to study colloid formation and with MVST waste as an analogue to wastes at other DOE sites. These techniques are in the advanced development stage and could also be easily incorporated into evaluations of ESW at further stages of development.

## **BENEFITS**

Advantages of alternative approaches to alkaline sludge washing would be to improve the effectiveness of dissolution thereby significantly reducing the volume of HLW glass produced. Alternative techniques would also reduce the amount of alkaline solution required as well as the volume of residual solution to be treated as LLW.

A preliminary cost analysis of ESW for Hanford wastes indicates cost savings of several billion dollars may be realized based upon the reduced volume of

HLW glass produced. Cost savings are also expected to be realized from reducing the volume of wash solutions, recycling chemicals, and reducing LLW disposal volume.

Another benefit of developing a successful ESW procedure is not having to develop and implement acid-side processing of sludges.

### **COLLABORATION/TECHNOLOGY TRANSFER**

Ultrasonic equipment from an industrial vendor will be evaluated as an alternative to ESW. This work involves bench-scale testing with actual waste that is necessarily carried out in specialized laboratories and hot cells at DOE facilities. Collaborators for the sludge treatment studies include theoretical determinations of silica behavior by researchers at Pennsylvania State University, and consultation on aluminum solubility from experts in the aluminum industry.

### **ACCOMPLISHMENTS**

- ORNL sludge treatment studies were funded in FY95 under the Efficient Separations and Processing Crosscutting Program.
- Gel formation was observed after acid leaching of MVST sludge; caustic leaching of MVST sludge was marginally effective in removing aluminum.

### **TTP INFORMATION**

Enhanced Sludge Washing Alternatives for Hanford Wastes and Sludge Treatment Studies technology development activities are funded under the following technical task plans (TTPs):

TTP No. RL36WT41, "Subtask 1 - Alternative Alkaline Washes of Hanford Sludges"

TTP No. OR16WT41, "Subtask 3 - Sludge Treatment Studies"

TTP No. OR16WT41, "Subtask 4 - Partitioning of Sludge Components by Caustic Leaching"

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### 3.3

## ACIDIC CESIUM/STRONTIUM/TRANSURANIC/ TECHNETIUM REMOVAL AT IDAHO

### TECHNOLOGY NEED

Approximately 1.8 million gallons of acidic liquid waste are stored in single-shell, stainless steel, underground storage tanks at the Idaho National Engineering Laboratory (INEL). In 1992, a Notice of Noncompliance was filed stating that the tanks did not meet secondary containment requirements of the Resource Conservation and Recovery Act (RCRA). Subsequently, an agreement was reached between DOE, the Environmental Protection Agency (EPA), and the Idaho Department of Health and Welfare that commits DOE to remove the waste from all underground tanks by the year 2015. Recent discussions with the state of Idaho have accelerated this date to 2012.

The baseline treatment for INEL liquid wastes produced after 2012 is the Full Treatment Option, wherein actinides and fission products will be removed from the liquid waste and HLW calcine. The depleted stream will be processed to Class A LLW standards and the radionuclides will be immobilized in an HLW fraction.

The Transuranic Extraction (TRUEX) process for removal of actinides, or transuranics, from acidic wastes has been tested with simulated wastes but has not been demonstrated on actual INEL waste in continuous countercurrent process equipment. The Strontium Extraction (SREX) process shows promise for co-extraction of strontium and technetium but also has not been demonstrated on INEL waste in continuous countercurrent operation. Both processes need to be evaluated on actual waste under continuous-flow solvent extraction conditions.

### TECHNOLOGY DESCRIPTION

The TRUEX process, originally developed by Horwitz and Schulz, has been tested in laboratories across the DOE complex for the past ten years or more. It is a solvent extraction process in which the complexing agent, CMPO, is dissolved in an organic carrier solvent and contacted with the acid stream in highly efficient centrifugal contactors. Typically, multiple contactors are connected in series; several stages are required to extract the transuranics and additional stages are used to strip them back into an aqueous phase.

The process has been under development at INEL for the past three years using simulants and spiked simulants in a centrifugal contactor pilot plant. The TRUEX process has been developed to the point where it is nearly ready for large scale application for the treatment of actual waste. However, prior to the

design of a facility utilizing the TRUEX process, it must be demonstrated in actual equipment using real waste.

In FY96 the process is being tested at INEL using a 24-stage bank of 2 cm centrifugal contactors and a sample of actual waste from INEL tanks (see Figure 3.3-1). The system is being installed and operated in a hot cell. The system will be operated continuously until reaching steady state, at which time each stage and exit stream will be sampled to determine concentration profiles and distribution coefficients for all 24 stages. The overall goal will be to determine whether the process will be able to reduce the transuranic concentration below the Class A LLW limit of 10 nCi/g.

In FY97, the SREX process will be demonstrated on actual tank waste using the centrifugal contactor mockup in the hot cell. This test will be focused on the removal of strontium, technetium, and possibly some RCRA toxic metals. SREX uses a crown ether extractant with tributyl phosphate in an organic solvent. The goal of this work will be to reduce the strontium content in the immobilized low-level waste fraction to below 0.04 Ci/m<sup>3</sup>.

These technologies are in the advanced development stage and are transitioning into the engineering development stage, where the data needed to support engineering design of a treatment facility will be developed. The subsequent stages of large scale demonstration and implementation would be integrated with design, construction, and startup of the treatment facility.

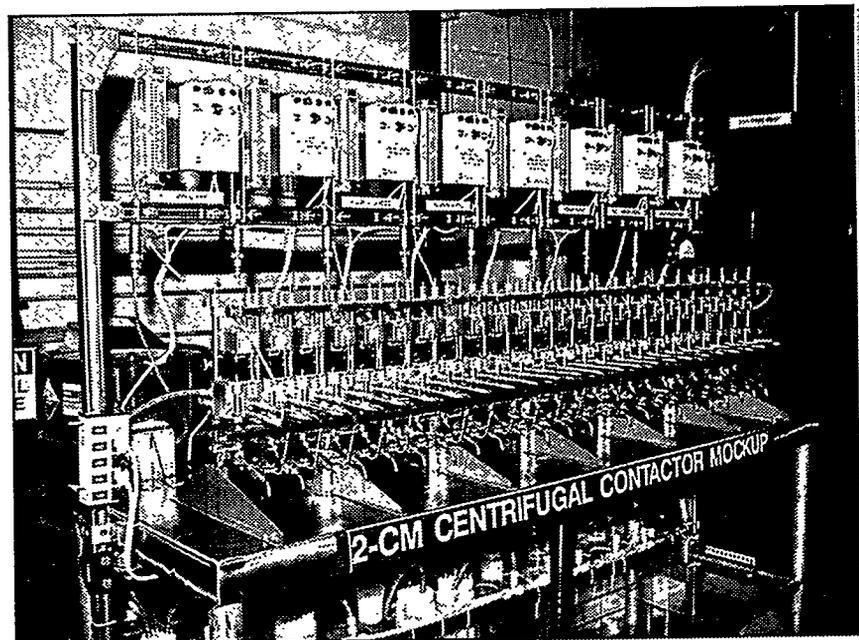


Figure 3.3-1. A centrifugal contactor test unit is being tested at INEL.

## **BENEFITS**

The benefits of successfully demonstrating the TRUEX process for remediation of HLW in tanks at INEL will be to provide engineering data for design of a treatment facility for waste currently stored in noncompliant tanks and to greatly reduce the volume of HLW for ultimate disposal.

Another benefit of testing TRUEX on actual waste will be to provide data on removing transuranics from actual HLW that may be useful to Hanford in determining whether acidic processing can be used to treat acidified Hanford sludge (TPA Milestone M 50-03). Also, the extraction equipment will be available for testing with acidified Hanford sludge if samples can be made available and transported to INEL for testing.

## **COLLABORATION/TECHNOLOGY TRANSFER**

The TRUEX and SREX processes were developed at Argonne National Laboratory (ANL). The extraction reagents are currently produced commercially by a specialty chemical producer and are available if a production scale process is needed.

The user-developer-producer team concept is being used to ensure technology transfer. The user is EM-30 ID, and the developers are INEL and ANL. This task is being co-funded by EM-30 at INEL. ANL is participating in this effort by assisting with test plans, providing support for the operation of the centrifugal contactor system, and assisting with the data analysis. The equipment being used is commercially available and the chemical extractants (CMPO and 18-crown-6) are available from Alf-Autochem and Eichrome industries respectively.

This task represents transfer of a technology developed within the Efficient Separations and Processing (ESP) Crosscutting Program to the TFA to ensure deployment of the TRUEX and SREX processes at Idaho.

## **ACCOMPLISHMENTS**

- This is a new task in the TFA, however, much work was completed under EM-30 sponsorship to bring the TRUEX and SREX processes to the point where they are ready for demonstration.
- Extensive tests were completed with simulated wastes using radioactive tracers as well as simulants with radioactive surrogates in 5.5 cm centrifugal contactor units.

## **TTP INFORMATION**

Acidic Cs/Sr/TRU/Tc Removal at Idaho technology development activities are funded under the following technical task plan (TTP):

TTP No. ID76WT41, "INEL Pretreatment"

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## 3.4 CESIUM REMOVAL

### TECHNOLOGY NEED

DOE's underground storage tanks at Hanford, Savannah River, Oak Ridge, and Idaho contain liquid wastes with high concentrations of radioactive cesium. Cesium is the primary radioactive constituent found in alkaline supernatant wastes. Since the primary chemical components of alkaline supernatants are sodium nitrate and sodium hydroxide, the majority of the waste could be disposed of as LLW if the radioactivity could be reduced below Nuclear Regulatory Commission (NRC) limits. Technology is needed to efficiently remove cesium from alkaline supernatants and concentrate it for eventual treatment and disposal as HLW. There are several new sorbents available which have shown high capacity and selectivity for cesium under highly alkaline conditions. These materials have been tested with simulated wastes and in small scale laboratory tests with actual wastes. These materials must be demonstrated at a larger scale with actual waste to assess their cesium separation performance and operational reliability.

The new Federal Facility Agreement (FFA) between DOE, EPA, and the Tennessee Department of Environmental Compliance will require cesium removal as mandatory treatment for ORNL supernatants prior to treatment and disposal as LLW. The Cesium Removal Demonstration is a major performance objective for the TFA and is included in a list of technologies agreed to be demonstrated in 1996 between President Clinton and Secretary O'Leary.

At Hanford, cesium must be removed to a very low level ( $3 \text{ Ci/m}^3$ ) to allow supernatant waste to be treated as LLW and disposed of in a near-surface disposal facility. The revised Hanford FFA and Consent Order, or Tri-Party Agreement (between DOE, EPA, and the Washington State Department of Ecology) also recommends treatment of LLW in a contact-maintained or minimally shielded vitrification facility to speed remediation and reduce costs. Cesium removal performance data are needed to estimate dose rates for this process and provide input to the design of an LLW pretreatment facility for Hanford supernatants.

At Savannah River, cesium removal by ion exchange may be needed as an alternative to the current in-tank precipitation (ITP) process. Cesium ion exchange may also be needed to separate cesium from Defense Waste Processing Facility (DWPF) recycle, or offgas condensate, to greatly reduce the amount of cesium that is routed back to the waste storage tanks.

## TECHNOLOGY DESCRIPTION

There are two cesium removal activities sponsored by the TFA in FY96. The first is an engineering scale demonstration of a modular cesium ion exchange unit using actual waste from the MVSTs at Oak Ridge. The second is laboratory scale testing of high efficiency cesium absorbers using actual waste from a Hanford tank.

The ORNL cesium removal demonstration will separate radioactive cesium from up to 25,000 gallons of MVST waste supernatant using a modular, mobile ion exchange system (see Figure 3.4-1). One objective is to demonstrate the use of a modular system thereby reducing capital costs associated with a large-scale, highly shielded pretreatment facility. Existing facilities at ORNL will be relied upon for secondary containment, process ventilation, utilities, and other services. ORNL will demonstrate decontamination of the unit to allow contact maintenance as well as transportation to another DOE site for possible re-deployment.

A high capacity ion exchange material, IE-911, was selected for use in the ORNL demonstration. This material is the engineered form of crystalline silicotitanate co-developed by Sandia National Laboratories and the UOP Corporation under a cooperative research and development agreement (CRADA). The sorbent was selected based on its effectiveness in laboratory scale tests including batch equilibrium tests and continuous flow column runs

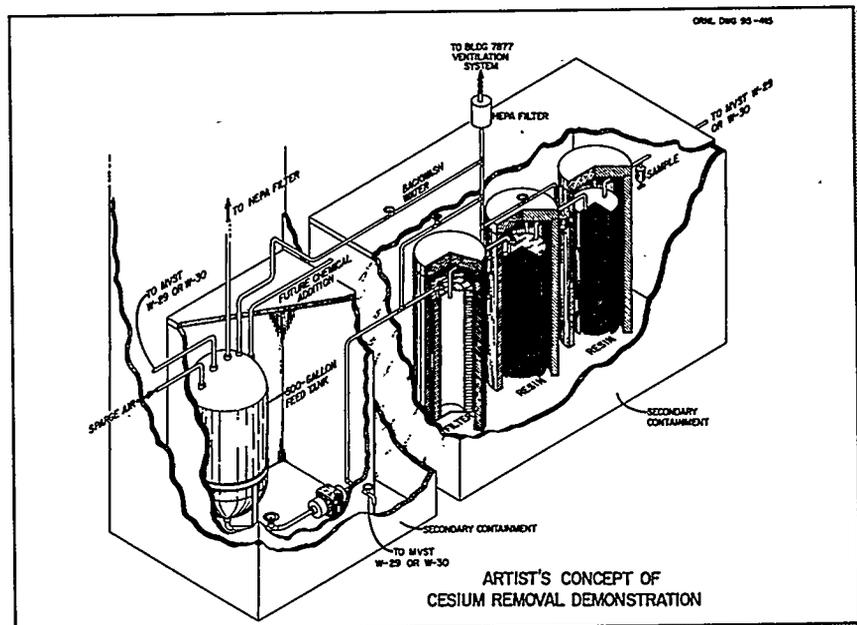


Figure 3.4-1. The cesium removal demonstration will feed waste through a filter tank and two resin tanks.

with both simulated and actual wastes. Several state-of-the-art cesium sorbents were evaluated including materials developed under sponsorship of the TFA, the ESP crosscutting program and EM-30 programs at the different DOE tank sites.

Cesium removal testing with actual Hanford waste will involve laboratory scale testing of a select number of high-performance cesium sorbents in continuous flow column tests similar to the work done at ORNL in FY95 using the MVST waste. The primary difference will be the use of actual Hanford supernatant. The testing will be done at Hanford since it is not feasible to transport the large quantities of supernatant needed to another lab for testing.

The results of the cesium testing on Hanford supernatant will be useful for development of process flowsheets for the treatment of Hanford wastes. Preliminary flowsheets have already been developed based upon predicted performance of cesium sorbents with several supernatant waste types. Process flowsheet calculations will be used as a basis for design of the cesium ion exchange system which will be the primary component of LLW pretreatment at Hanford.

The cesium removal testing with Hanford supernatants is in the advanced development stage in that it involves laboratory bench-scale testing with actual waste. Tests will be run this year with a sample of Hanford Double Shell Slurry Feed (DSSF). If possible, it would be desirable to test complexant concentrate and dissolved saltcake wastes to observe possible variations in sorbent performance. Two sorbents will be tested, resorcinol-formaldehyde (R-F) resin and crystalline silico-titanate inorganic ion exchanger. There are other sorbents available that could be evaluated in this stage of development, particularly the regenerable class of exchangers like the R-F resin.

## **BENEFITS**

Without cesium removal, an overwhelmingly large volume of waste would have to be treated and disposed of as HLW. Cesium removal will enable reclassification of waste to LLW which can be treated and disposed of at a fraction of the cost of HLW, and highly efficient cesium removal will greatly reduce radiation exposure hazards to the environment during treatment and disposal of the waste.

## **COLLABORATION/TECHNOLOGY TRANSFER**

The cesium removal demonstration has been coordinated closely with other DOE technology development projects including those sponsored by the TFA, ESP, and site EM-30 organizations. This has resulted in a comprehensive set of sorbents being evaluated for eventual down-selection to the preferred

material chosen for the first demonstration run, IE-911. The possibility of an additional demonstration run in FY97 with a second ion exchange material presents opportunities for industry and universities in development of improved sorbent and modeling data from bench-scale to full-scale systems. The IE-911 development itself was the result of a collaboration between a national laboratory (Sandia) and an industrial partner (UOP). The demonstration unit was designed and fabricated by a commercial vendor.

### ACCOMPLISHMENTS

Several major milestones were completed during FY95 for the cesium removal demonstration at ORNL:

- Completion of a design alternatives report
- Assembly of a cold test loop and initial testing with resorcinol-formaldehyde resin
- Specifications for design and construction of the ion exchange system
- Placement of a contract for design and construction of the cesium removal demonstration system

### TTP INFORMATION

Cesium Removal technology development activities are funded under the following technical task plans (TTPs):

TTP No. OR16WT41, "Subtask 2 - Cesium Removal Demonstration"

TTP No. RL46WT41, "Subtask 1 - Cesium Tests with Actual Hanford Supernatants"

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### 3.5

## TECHNETIUM REMOVAL STUDIES ON HANFORD WASTE

### TECHNOLOGY NEED

Technetium (Tc)-99 has a long half-life (210,000 years) and is very mobile in the environment when in the form of the pertechnetate ion ( $\text{TcO}_4^-$ ). Removal of Tc from alkaline supernatants and sludge washing liquids is expected to be required at Hanford to permit treatment and disposal of these wastes as LLW. The disposal requirements are being determined by the long-term performance assessment of the LLW waste form in the disposal site environment. It is also expected that Tc removal will be required for at least some wastes to meet NRC LLW criteria for radioactive content. To meet these expected requirements, there is a need to develop technology that will separate this extremely long-lived radionuclide from the LLW stream and concentrate it for feed to HLW vitrification.

### TECHNOLOGY DESCRIPTION

The technical approach to Tc removal is to determine the amount of Tc present in the waste, determine what fraction is present as the pertechnetate anion, test available sorbents with actual Hanford waste samples, and use the results to predict Tc removal for the Hanford TWRS process flowsheet. Tc removal will most likely be deployed after cesium removal for alkaline supernatants and sludge wash liquids. The decontaminated liquid waste would be treated for disposal as LLW and the Tc-rich stream would be sent to HLW treatment for vitrification. Pertechnetate removal would be accomplished using strong base anion exchange in continuous flow columns. Several sorbents are available from industry while others have been developed as part of the ESP program. To get maximum Tc removal, an oxidizing agent would be added to the waste feed to convert all of the Tc to the pertechnetate form prior to ion exchange. Multiple ion exchange columns would be used to allow continuous loading while a loaded column is being eluted off line. The concentrated eluant containing the pertechnetate would be routed to HLW treatment.

Two complementary and closely coordinated tasks are involved with evaluating Tc removal from Hanford waste. First, batch testing is being performed by PNNL in a protocol designed to determine how much Tc is present in the waste in pertechnetate form, and possibly how other treatment steps such as cesium removal may affect the form. Second, several commercially-available Tc sorbents are being evaluated in column tests with actual waste which has undergone cesium removal. Columns are being selected and prepared by LANL and Argonne and the evaluations are being done by PNNL. This work is

in the advanced development stage since these are bench-scale tests for a specific application. The next stage of development will be engineering scale, which could be performed with actual waste, simulated waste spiked with radioactive tracer, or simulated waste with nonradioactive surrogates for the technetium.

## **BENEFITS**

This technology will greatly reduce the volume of waste to be disposed of as HLW. This benefit will depend directly upon the performance assessment's determination of how much total Tc can be disposed of in LLW. The technology will also reduce the technical risk of Phase I privatization of LLW treatment at Hanford since the technology has not been proven on Hanford waste. Because of these factors and the limited development to date, Tc removal is considered a high priority need.

## **COLLABORATION/TECHNOLOGY TRANSFER**

The Hanford EM-30 TWRS program has a comparable effort underway this year to test Tc removal using sodium sulfide as a precipitant. There are also TWRS activities addressing volatility of Tc in HLW treatment and the use of sorbents at the disposal site to prevent migration of Tc. The data developed through each of these activities will be used by the TWRS flowsheet development group to predict the extent of Tc removal needed and the performance of the proposed ion exchange process. This work will also take advantage of Tc sorbent development work carried out in previous years under the ESP Crosscutting Program.

## **ACCOMPLISHMENTS**

As this is a new initiative, accomplishments will be discussed in future issues of this publication.

## **TTP INFORMATION**

Tc Removal Studies on Hanford Waste technology development activities are funded under the following technical task plans (TTPs):

TTP No. RL36WT41, "Subtask 4 - Tc Removal Studies on Hanford Waste"

TTP No. AL16WT41, "Subtask 2 - Tc Removal Studies"

TTP No. CH26WT41, "ANL Pretreatment"

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## 3.6

# MOBILE EVAPORATOR DEMONSTRATION

### TECHNOLOGY NEED

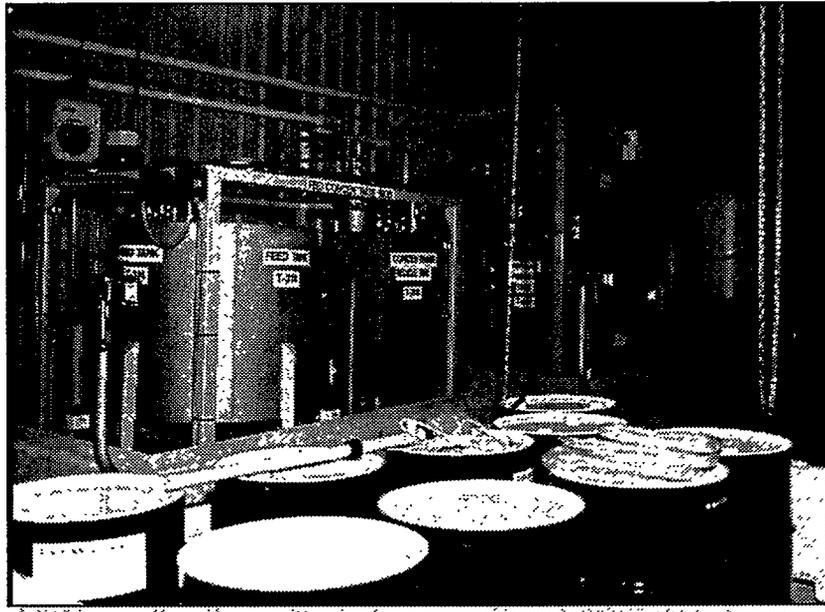
This project addresses a need to conserve waste tank storage space at Oak Ridge. Only the double-shell tanks at ORNL are in compliance with the FFA between DOE, EPA, and the Tennessee Department of Environmental Compliance. Evaporators offer the possibility of removing water from tank waste, thus making space available in the double-shell tanks, so waste from noncompliant tanks can be moved to compliant tanks. The alternative to evaporation would be to remove and solidify the waste from the noncompliant tanks, producing a waste form for which there is currently no permitted storage at ORNL.

Hanford, Savannah River, and Oak Ridge will also add excess water to tank waste as a consequence of sludge retrieval activities, sludge washing, and decontamination activities. Evaporation may be used to remove the excess water to conserve tank storage space, reduce the volume of the final waste form, and reduce the water-removal load of high-temperature sludge treatment processes such as vitrification.

### TECHNOLOGY DESCRIPTION

The TFA is developing an evaporator to remove excess water from ORNL waste. A demonstration will be conducted in which 25,000 gallons of liquid LLW supernate from the MVSTs will be processed, reducing the volume to 19,000 gallons and freeing up 6,000 gallons of tank space. This technology will demonstrate mobile deployment of an evaporator system and decontamination performance of the system using actual waste. The skid-mounted evaporator unit will be installed and operated in an existing facility with temporary shielding (see Figure 3.6-1). After waste processing, the unit will be decontaminated for hands-on maintenance and transport. The overhead condensate (the water removed from the waste) is expected to be extremely low in radioactivity and can be discharged to the ORNL process waste treatment plant for removal of trace contaminants and discharge of water to the environment.

Evaporator technology has been used extensively in commercial industry to efficiently remove water from liquid solutions for many years. Evaporators have also been used for many years to reduce the volume of radioactive wastes stored in tanks at DOE facilities. One of the most common applications is to process very dilute waste streams achieving very high waste volume reductions (often > 90 percent) and conserving large volumes of tank space.



GF96-0161

**Figure 3.6-1.** The evaporator unit will be installed and operated in an existing facility.

For this demonstration, the waste composition is essentially a 4 to 5 molar sodium nitrate salt solution contaminated with radioactive cesium-137 and strontium-90 at activities of 8 mCi/L and 0.2 mCi/L respectively. The objective will be to evaporate the waste to a level approaching the solubility limit of the dissolved salts. The evaporator is designed to operate at reduced pressure (sub-atmospheric) similar to vacuum distillation which will also reduce the boiling point of the solution and allow more water to be drawn off at a lower temperature.

This project will produce performance data such as processing capacity and decontamination factors for radioactive constituents. The demonstration will identify special operational and maintenance issues for mobile process units and evaluate the feasibility of decontaminating the system to allow hands-on maintenance and transportability to another site. Finally, the demonstration on actual waste will evaluate the relationship between the performance of pilot-scale evaporators processing surrogate waste solutions and a full-scale evaporator processing actual waste.

This technology demonstration is full scale for treatment of waste from medium-sized waste storage tanks such as the MVSTs at ORNL and is also considered full scale as a concentration process step in a waste treatment plant at Savannah River or Hanford. Completion of the Mobile Evaporator Demonstration is a full-scale demonstration performance metric for the TFA during FY96 and is included in a list of technologies agreed to be demonstrated in 1996 between President Clinton and Secretary O'Leary.

## **BENEFITS**

This project will demonstrate the design and operation of a mobile, skid-mounted, sub-atmospheric-pressure evaporator for concentrating radioactively contaminated, high salt content waste from ORNL underground storage tanks. The decontamination factor achieved and feed processing rate achieved will be useful to those developing process flowsheets for waste treatment at other DOE sites.

The benefit of this demonstration is that volume reduction of the waste at ORNL will make space available in the double-shell tanks allowing waste to be moved from noncompliant storage tanks to environmentally compliant tanks.

Large-scale and stationary evaporator facilities are also in use at other DOE sites including two Tank Farm Evaporators at Savannah River and the 242-A Evaporator at Hanford. Processing facilities such as the DWPF also use evaporation as an integral part of the waste treatment process. Pretreatment processing of alkaline liquid wastes at Hanford will likely require a dilution step before cesium removal for some wastes. These waste streams may then need to undergo volume reduction prior to treatment to reduce LLW feed storage tank volume requirements and reduce the amount of water to be processed during LLW vitrification. It would be beneficial to have an evaporator that would process only LLW feed to avoid the possibility of cross-contamination with HLW streams that are routinely processed in the large-scale evaporators.

## **COLLABORATION/TECHNOLOGY TRANSFER**

This demonstration is a collaboration with the ORNL Waste Management Remedial Action Division, which is providing equivalent funding for the work. At the completion of the demonstration, the process is expected to be transferred to EM-30 for future production use.

The previous year's development involved two smaller scale evaporator systems with collaboration by industry vendors. The full-scale evaporator unit is being acquired from industry; Delta Thermal Systems, Inc. was awarded the procurement last year as a result of a competitive bid.

## **ACCOMPLISHMENTS**

Several milestones for activities leading up to the actual hot demonstration of the mobile evaporator unit were completed in FY95:

- An engineering feasibility study defining technical requirements and cost estimate was completed.

- Technical specifications for the purchase of the evaporator system were developed.
- A purchase contract was awarded and fabrication of the system was initiated.
- The system was delivered to ORNL, installed, and cold tested early in FY96.

### **TTP INFORMATION**

Mobile Evaporator Demonstration technology development activities are funded under the following technical task plan (TTP):

TTP No. OR16WT41, "Subtask A - Mobile Evaporator Demonstration"

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## 3.7 SOLID/LIQUID SEPARATIONS

### TECHNOLOGY NEED

A number of liquid streams encountered in tank waste pretreatment contain fine particulate suspended solids. These streams may include tank waste supernatant, waste retrieval sluicing water, and sludge wash solutions. Other process streams with potential for suspended solids include evaporator products and ion exchange feed and product streams. Suspended solids will foul process equipment such as ion exchangers. Radioactive solids will carry over into liquid streams destined for LLW treatment, increasing waste volume for disposal and increasing the need for shielding of process equipment. Streams with solid/liquid separation needs exist at all of the DOE tank waste sites.

A variety of solid/liquid separations techniques have been used in the chemical process industries that could have application to the specific problems encountered with DOE radioactive tank wastes. The particular method selected will depend upon characteristics of the waste, process parameter constraints, and adaptability of process equipment to the radioactive environment.

### TECHNOLOGY DESCRIPTION

This work consists of three tasks at three sites. The Solid/Liquid Test Equipment Development and Transfer activity conducted at Savannah River is directed at evaluating solid/liquid separation techniques applicable to several waste streams and pretreatment processes at the DOE tank sites. Several separation techniques are considered for any given application including in-tank settling, clarifiers, hydrocyclones, cartridge filters, and crossflow filters. A specific objective of this work is to evaluate commercially available crossflow filtration equipment applicable to several needs across the DOE complex (see Figure 3.7-1).

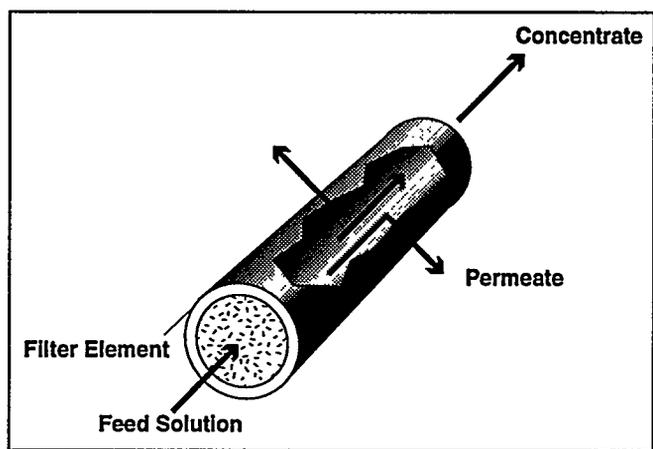


Figure 3.7-1. An instrumented unit will use the physical principle of crossflow filtration.

An instrumented crossflow filtration unit, scaled up four times from previous testing, is being used with simulated wastes to predict performance with radioactive wastes and evaluate rheological parameters that could affect operations. The data are being used to predict whether crossflow filtration will be applicable for the variety of solids/colloids expected from washing of Hanford sludges. During waste retrieval, the sludge will be suspended with large volumes of water causing the sludge volume to increase. Volume reduction of the washed sludge solids would reduce tank space required for interim storage prior to HLW vitrification. Testing will determine the effect of slurry composition on filter performance. A sludge washing demonstration will be performed.

The Crossflow Filtration Testing on Hanford Wastes task will use a duplicate crossflow filtration unit from Savannah River for testing on liquid streams from sludge washing tests of Hanford wastes. Conditions will be chosen to determine whether the process is suitable for performing bulk separations in lieu of the baseline settle/decant process. This technique will also be evaluated for clarifying supernatant prior to cesium ion exchange. Testing with actual waste will determine how well the process will perform under continuous operating conditions and will provide engineering data useful for process design.

Solid/Liquid Separation of Suspended Solids from Gunite Tanks: This task selects the best filtration technique for solids expected in the waste stream generated by sludge heel removal from the Gunite tanks at ORNL. Simulants are used to compare techniques in collaboration with the Savannah River task. ORNL will also use one of the small-scale duplicate crossflow filter units to test actual samples of Gunite tank sludges.

## **BENEFITS**

The primary benefits of applying appropriate solid/liquid separations technology will be efficient solids removal, repeatable performance, and reliable operation of the equipment. A direct positive effect will be improved quality of the liquid LLW product such that overall waste volume is minimized. Fouling of process equipment will be minimized and the useful life of ion exchange resins will be extended. Radiation exposure to operators and maintenance crews in LLW treatment steps will be reduced.

## **COLLABORATION/TECHNOLOGY TRANSFER**

Research on various types of crossflow filters has been ongoing at Savannah River for more than a decade. The experience gained is being transferred to Hanford and Oak Ridge. The correlation between laboratory testing and the full scale In-Tank Precipitation process will be transferred to other sites to use in developing scale-up factors for solid/liquid separations processes at their

sites. The solid/liquid separations equipment used for testing is obtained from commercial sources. Vendors are being consulted for their experience with similar problems in non-DOE applications. If applicable, commercial vendors will perform evaluations of technologies on a contract basis.

### **ACCOMPLISHMENTS**

- Tests were conducted using various commercially available crossflow filters and waste simulants.
- Various waste stream solid/liquid separation techniques were reviewed for applicability.

### **TTP INFORMATION**

Solid/Liquid Separations technology development activities are funded under the following technical task plans (TTPs):

TTP No. SR16WT41, "Subtask 1 - Solid/Liquid Test Equipment Development and Transfer"

TTP No. RL36WT41, "Subtask 2 - Crossflow Filtration Testing on Hanford Wastes"

TTP No. OR16WT41, "Subtask 5 - Solid/Liquid Separation of Suspended Solids from Gunite Tanks"

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## 3.8 COUNTERCURRENT DECANTING

### TECHNOLOGY NEED

Sludge at Savannah River, Hanford, and Oak Ridge will be washed to remove soluble components prior to HLW vitrification. Removing suspended solids from the wash solutions is inherently inefficient due to long time intervals required for the solids to settle out. The baseline process for sludge washing at Savannah River and Hanford is done batchwise in large, one-million gallon underground storage tanks. This requires large volumes of wash solution, powerful mixing pumps, and long settling times. Retrieval of waste using large volumes of dilution water is planned at Hanford. To consider the benefits of flocculent addition and the possibility of using countercurrent decantation to help optimize sludge washing, the settling characteristics of the solids need to be determined.

### TECHNOLOGY DESCRIPTION

This commercial industry technology is being considered for adaptation to HLW treatment as a method to more efficiently wash sludges, decant the liquids, and concentrate the solids for further treatment. The technique, known as countercurrent decanting (CCD), uses a series of clarifiers to wash sludge in a cascade, concentrating the sludge in the final stage and producing a liquid stream out the other end with a very low solids content (see Figure 3.8-1). CCD is highly effective in washing solids because the wash water flows in the opposite direction relative to the solids. The size of the equipment is largely dependent upon the settling characteristics of the solids. However, settling

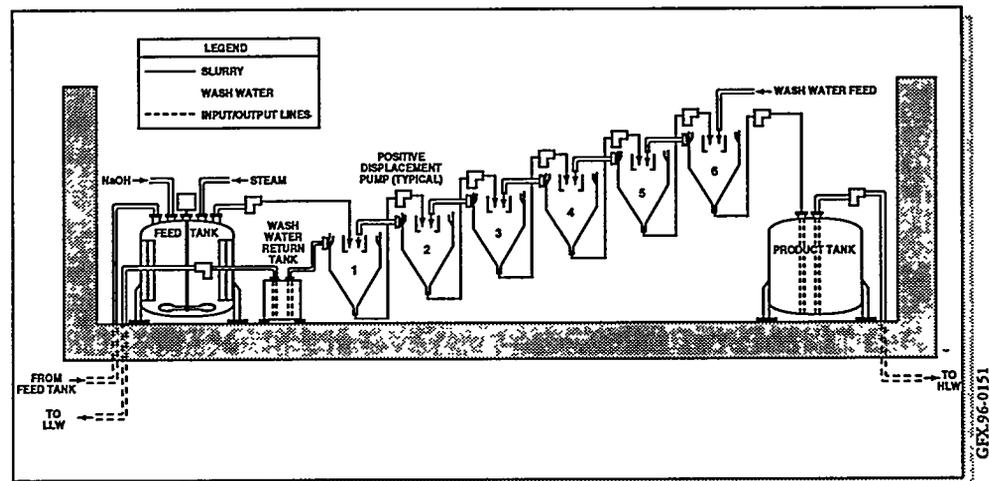
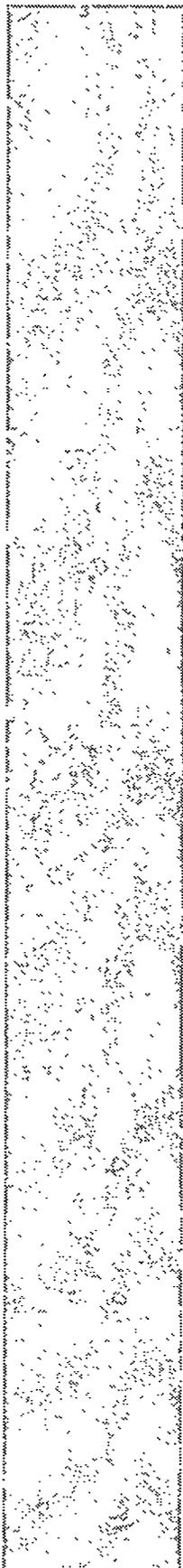


Figure 3.8-1. The CCD circuit uses a series of clarifiers.



characteristics will vary depending upon the composition and history of the solids, the salt concentration in the supernatant, and whether or not a flocculent is used.

Savannah River and Hanford baselines are to perform sludge washing in batch mode in large underground storage tanks. This technology is being evaluated to determine what advantages can be realized by reducing processing time and equipment volume (cost) over other alternatives.

The first step will be to evaluate existing solids settling data. Sludge washing tests have been performed at both Savannah River and Hanford. Tests show that settling is slower at high salt concentrations. Tests on Hanford waste samples indicate that settling rates vary widely from tank to tank, possibly due to varied chemical composition or possibly the thermal history of the tank. Additional tests on Hanford wastes may be needed in order to come up with a CCD design for washing Hanford sludge.

The next step will be to select a sludge simulant and identify a suitable flocculent. Settling data from Savannah River sludges and sludge simulants will be compared to ensure that a representative simulant can be selected that has settling characteristics that match actual waste. Settling tests will be run on Savannah River tanks that have had high temperatures in the past to determine whether the one simulant can be used to represent all of the tanks. Based on results of flocculent testing at Hanford in FY95 (a minimum of eight tanks were tested), tests will be run to select an optimum flocculent for use with sludges from Savannah River tanks.

Testing will be initiated with an industrial partner to develop a process flowsheet for sludge washing with a CCD system. The industrial partner will perform tests on the simulant to gather the necessary data. Settling rates will be determined under a variety of conditions including different salt concentrations and flocculent. Once the settling rate data are obtained, the process equipment can be specified and a cost estimate developed.

This technology is currently being used in commercial industry. The feasibility of its application to HLW sludge processing, based upon settling rates of simulated sludges and process flowsheet calculations, is the scope of this year's work. If found favorable, the next phase would be to demonstrate the technology on a small scale using actual waste. A pilot-scale system could then be designed for testing with simulants. The next stage would be full-scale implementation using simulants to test the equipment prior to testing with actual waste.

## **BENEFITS**

Countercurrent decanting is a technique used in other industries to efficiently handle solids washing. The technique would reduce the volume of wash water used and reduce the required size of special sludge washing tanks. Benefits of improved technology include reduction of overall HLW volume, lower overall processing time, smaller equipment volume, and lower volumes of wash solution required.

## **COLLABORATION/TECHNOLOGY TRANSFER**

An industry partner will be sought for the evaluation phase to test DOE waste simulants with a flocculent. A following phase will be a demonstration of the technology on actual DOE waste.

This work relies heavily on the input of industrial partners. The information from the vendors is being shared with Hanford and Oak Ridge.

## **ACCOMPLISHMENTS**

As this is a new initiative, accomplishments will be discussed in future issues of this publication.

## **TTP INFORMATION**

Countercurrent Decanting technology development activities are funded under the following technical task plan (TTP):

TTP No. SR16WT41, "Subtask 2 - Countercurrent Decanting"

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### 3.9

## CAUSTIC RECOVERY AND RECYCLE

### TECHNOLOGY NEED

Baseline sludge washing processes at both Hanford and Savannah River call for large volumes of caustic (sodium hydroxide) solution. The supernatant from sludge washing then becomes feed to LLW treatment. The added caustic can be recovered after washing and recycled to subsequent sludge washing steps. In addition, the HLW sludges at Hanford and Savannah River contain large quantities of sodium salts that can, in principle, be recovered as sodium hydroxide and also be recycled.

### TECHNOLOGY DESCRIPTION

Technology exists to remove sodium ions from a liquid stream with high salt content and reconstitute them as pure sodium hydroxide in aqueous solution. This technique is known as electrochemical salt splitting and is accomplished with the use of membranes that selectively allow transport of sodium ions while preventing the transfer of other components in solution.

This technology basically avoids the need to use fresh sodium hydroxide solutions as corrosion inhibitors, and for caustic leaching of HLW sludges, by removing the sodium already present in the waste and using it to pre-treat subsequent batches of sludge.

The technology being developed uses ion-selective membranes in an electrochemical cell to separate sodium ions from a mixture of salts such as would be found in liquid wastes from sludge washing and alkaline supernatants (see Figure 3.9-1). If complete regeneration of sodium hydroxide

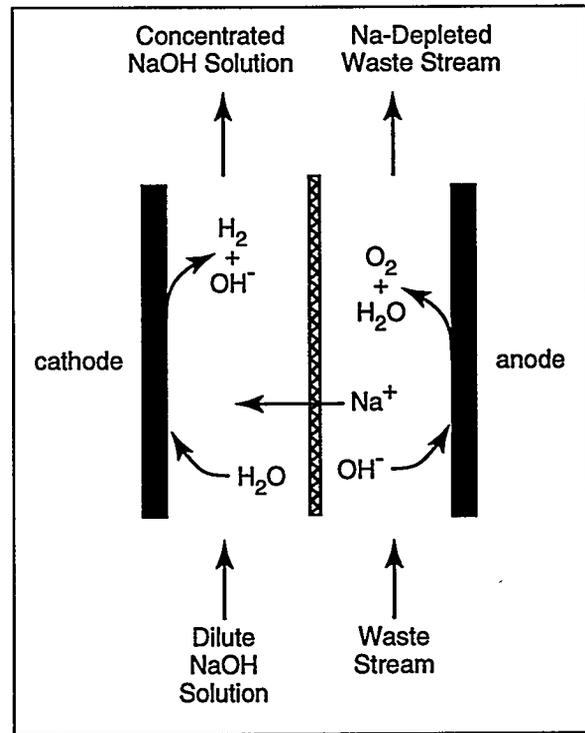


Figure 3.9-1. Caustic recovery by electrochemical salt splitting uses ion-selective membranes.

from sludge washing liquids were practical, the sodium could theoretically be regenerated indefinitely. This is not possible. However, tank waste supernatants typically contain a minimum of 5 moles per liter of sodium. Sludge washing is done with 3 moles per liter sodium and the overall volume is smaller than that required for sludge washing.

In salt splitting, ions are transported across the membrane into a fresh aqueous solution where sodium hydroxide is produced by splitting water. A variety of membranes have been developed for a number of industrial applications including chlorine/caustic production, desalination of sea-water, and advanced battery technology. This task is evaluating these classes of membranes to determine which will be best for electrochemical caustic recovery from alkaline waste streams.

Bench-scale testing is being initiated this year on simulated Savannah River waste. The results from this testing will be used in a preliminary conceptual design to evaluate the performance advantages and cost-effectiveness of implementing caustic recycle technology.

Electrochemical salt splitting is a well established industrial technology used in waste water treatment, water purification, and valuable chemical recovery processes.

## **BENEFITS**

By recycling caustic, little if any fresh sodium hydroxide would be needed to perform caustic leaching and water washing of HLW sludges. Currently, the wash liquids are treated as LLW. Recycling would substantially reduce the volume of LLW produced.

It has been estimated that the amount of LLW to be produced in the baseline sludge washing process at Hanford will be increased by 13 to 16 percent as a result of the addition of fresh caustic. Thus, the overall potential cost savings by recovering and recycling caustic is on the order of \$100 million.

At Savannah River, the volume of LLW immobilized as saltstone could be reduced by up to 23 percent and the total life cycle cost savings have been estimated at \$25 million.

## **COLLABORATION/TECHNOLOGY TRANSFER**

This technology is being developed with the help of experts in electrochemical technology from industry, academia, and the DOE national laboratory system. Collaborators include the Electrosynthesis Company of Buffalo, New York; Dr. R. White at the University of South Carolina; and researchers at PNNL.

Private industry, DOE national laboratories, and other EM-50 activities are coordinating in the development of this technology.

### **ACCOMPLISHMENTS**

As this is a new initiative, accomplishments will be discussed in future issues of this publication.

### **TTP INFORMATION**

Caustic Recovery and Recycle technology development activities are funded under the following technical task plan (TTP):

TTP No. SR16WT41, "Subtask 2 - Caustic Recovery and Recycle"

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## 4.0

# WASTE IMMOBILIZATION OVERVIEW

Waste immobilization technology converts radioactive waste into solid waste forms which will last in natural environments for thousands to millions of years. Wastes requiring immobilization at DOE sites include low-level wastes (LLW) such as the pretreated liquid waste from waste tanks and the high-level wastes (HLW) such as the tank sludges. There are also a number of secondary wastes requiring immobilization that result from tank waste remediation operations, such as resins from cesium and technetium removal operations.

The baseline technologies to immobilize radioactive wastes from underground storage tanks at DOE sites include converting LLW to either grout or glass and converting HLW to borosilicate glass. Grout is a cement-based waste form that is produced in a mixer tank and then poured into canisters or pumped into vaults. Glass waste forms are created in a ceramic-lined metal furnace called a melter. Tank waste and dry materials used to form glass are mixed and heated in the melter to temperatures ranging from 1,800°F to 2,700°F. The molten mixture is then poured into log-shaped canisters for storage and disposal. The working assumption is that the LLW will be disposed of on site, or at the Waste Isolation Pilot Plant if transuranic elements are present. The HLW will be shipped for off-site disposal in a licensed HLW repository, such as the one proposed at Yucca Mountain, Nevada.

Feed preparation and melter processes for vitrifying ion exchange resins and other secondary wastes are being demonstrated. Additionally, cost and performance data on the processes required to produce grout and glass are being collected to guide DOE sites in the selection of the most appropriate technology and waste form for their baselines.

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## 4.1

# FORM FOR IMMOBILIZATION OF LOW-LEVEL WASTE

### TECHNOLOGY NEED

Two promising technologies and waste forms exist for treating LLW from radioactive waste storage tanks in the DOE complex: grout and glass. Selection of the final waste form at a DOE site depends on the processing, economic, and performance advantages of each. Testing and demonstrating the processes required to produce both of the waste forms will provide information to guide DOE sites in the selection of the most appropriate technology and waste form for their specific LLW application.

A number of site-specific needs are being addressed by this effort:

- Methods are needed to immobilize the LLW fraction resulting from the separation of radionuclides from the liquid and high-level calcine wastes at the Idaho National Engineering Laboratory (INEL). LLW is to be mixed with grout, poured into steel drums, and transferred to an interim storage facility, but alternatives are being considered.
- Oak Ridge is still making decisions regarding final disposition of LLW. Tests must be conducted with surrogate and actual wastes to support selection of a final waste form.
- The Savannah River Site (SRS) has selected saltstone grout (pumped to above ground concrete vaults and solidified) as the final waste form. Savannah River would like to evaluate LLW glass as an alternative to saltstone disposal.
- The Project Hanford Management Contract states that Hanford must construct and begin to operate an LLW commercial demonstration facility by June 1, 2002. A final waste form for LLW is not specified; however, stakeholders prefer LLW glass.

### TECHNOLOGY DESCRIPTION

Wastes from the Oak Ridge Bethel Valley Tank Farm will be both grouted and vitrified (see Figure 4.1-1) after the wastes have been retrieved and blended to homogenize the composition. These tanks are part of the 18 tanks at the Oak Ridge Site assigned to a Waste Area Grouping called Gunite and Associated Tanks (GAAT). The GAAT waste is being characterized and mobilized at Oak Ridge as a part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) treatability studies.

Waste will be grouted and vitrified in facilities at the Oak Ridge National Laboratory (ORNL). The stability of grout and glass waste forms produced using actual sludge will be compared, and the results of this comparison will be made available to site planners and stakeholders across the DOE complex. Two glass waste forms will be tested: borosilicate glass and iron phosphate glass.

The grout facility will be installed next to the Gunite tanks. Candidate vitrification systems for producing the glass waste form will be installed in the shielded cells facility near the Oak Ridge South Tank Farm or in a temporary shielded facility located near the Gunite tanks. The vitrification system will be either a conventional or stirred joule-heated melter, or a crucible furnace.

In FY96, design criteria for producing the glass waste form will be developed and vendors for small-scale grout and glass production will be selected. Also in FY96, the GAAT waste will be sampled and analyzed to finalize the chemical and radionuclide composition. Sample glass and grout formulations from actual GAAT waste will be prepared and tested in the laboratory. The specifications for the vitrification feedstock and the grout feedstock for small-scale tests will be prepared based on these laboratory tests and input solicited from other sites. In FY97, a small-scale demonstration of grout technology will be conducted and the melter will be designed and installed. In FY98 the small-scale demonstration of vitrification technology will be completed.

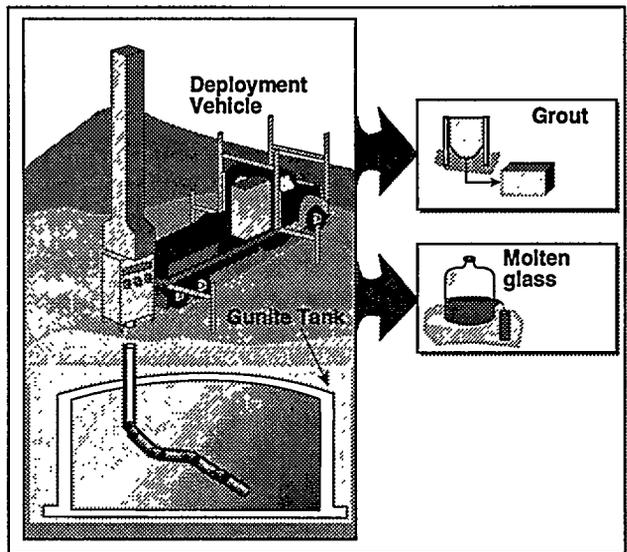


Figure 4.1-1. The stability of grout and glass waste forms produced in small-scale facilities operated by private contractors next to the Gunite tanks will be tested and compared.

## BENEFITS

The technology required to produce grout and glass waste forms is available, but the technology has been used on different waste streams or simulants. This will be the first demonstration of this technology on the same waste stream, so that the performance characteristics and costs of the waste forms and their associated production technologies can be compared. This study will enable DOE to understand the viability and stakeholder acceptability of the

waste forms produced, so that LLW immobilization technology can be selected and proceed to full-scale implementation at DOE sites.

Applying the two technologies (grout and glass) to the same waste stream will allow an unbiased appraisal of the true costs and risks associated with implementing each technology for full-scale tank waste remediation. Testing of the stability of the waste forms generated will better define the performance of both waste forms for both the short term and long term. The results will be accessible to stakeholders and widely applicable throughout the DOE complex to a broad spectrum of LLW, including sludge, solids, and supernates.

### **COLLABORATION/TECHNOLOGY TRANSFER**

The organizations involved in this task include Savannah River Technology Center (SRTC) and ORNL. ORNL is responsible for obtaining actual waste samples during the GAAT Treatability Studies. SRTC will provide technology and expertise for grouting and vitrifying the waste samples. Private companies will design and operate small-scale grout and vitrification facilities. If the stirred melter is selected for the vitrification system, a cooperative research and development agreement may supply new stirred melter technology to DOE users.

The project is funded by the DOE Office of Environmental Management. The results will be transferred to other DOE sites, private industry, and any other interested parties, as appropriate, through reports and conferences.

### **ACCOMPLISHMENTS**

- Glass formulation testing and vitrification system selection are underway, and vendors have been contacted for both vitrification systems and shielding.
- Borosilicate glass with 40 percent waste loading and iron-phosphate glass with 35 percent waste loading have been produced using waste surrogates, and product consistency tests have been initiated to assess the durability of the respective glass waste forms.

### **TTP INFORMATION**

Form for Immobilization of Low-level Waste technology development activities are funded under the following technical task plan (TTP):

TTP No. SRI6WT31, "WSRC Immobilization"

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## 4.2

# VITRIFICATION OF ION EXCHANGE RESINS

### TECHNOLOGY NEED

DOE sites at Hanford, Savannah River, INEL, and Oak Ridge will remove cesium from the hazardous radioactive liquid waste in the underground storage tanks. If cesium is removed, it costs less to treat the rest of the waste. However, cesium removal from tank waste, while cost-effective, creates a significant volume of solid waste that must be turned into a final waste form for ultimate disposal. The plan is to separate cesium from the liquid waste using ion exchange or other separations media, treat the cesium-loaded separations media to prepare it for vitrification, and convert the cesium product into a glass waste form suitable for final disposal. Personnel exposures during processing and the amount of hazardous species in the offgases must be kept within safe limits at all times.

The effectiveness of advanced oxidation technology for treating organic cesium-loaded separations media prior to vitrification is not proven. After a suitable melter feed is obtained, vitrification of the cesium-loaded media must be demonstrated. Technology development is needed because:

- Compounds are in the separation media that must be destroyed or they will cause flammability problems in the melter and decrease the durability and waste loading of the final waste form.
- High beta/gamma dose rates are associated with handling cesium-containing waste.
- Cesium volatilizes in the melter and becomes a highly radioactive offgas problem.

### TECHNOLOGY DESCRIPTION

The cesium-loaded separations media to be treated in this project are being obtained from the cesium removal demonstration (CsRD) project at the Oak Ridge Reservation in Tennessee. Waste retrieved from the Melton Valley Storage Tanks is being transferred to a small-scale cesium removal facility located next to one of the tanks. Radioactive cesium is captured on three candidate separation media: resorcinol-formaldehyde resin, an engineered form of crystalline silicotitanate, and hexacyanoferrate sorbers. Processing options for treating the separation media prior to vitrification include dissolving the cesium-loaded material and implementing advanced oxidation to destroy the hexacyanoferrate sorbers and the resorcinol-formaldehyde resins. Crystalline silicotitanites will be dissolved and directly incorporated into

the final waste form. A prototype installation of the oxidation system is set up in a hot cell at Argonne National Laboratory (ANL) for the initial testing of this technology (see Figure 4.2-1).

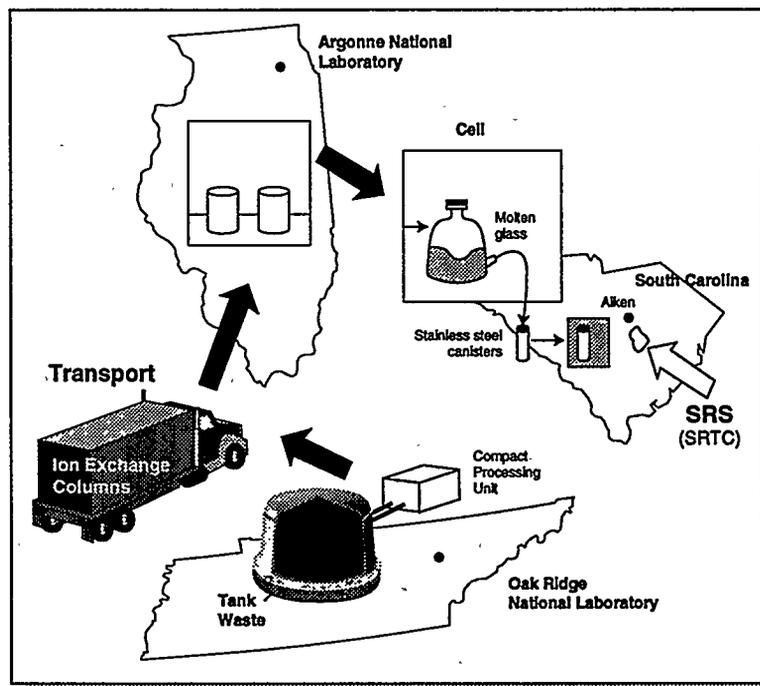


Figure 4.2-1. Cs sorbents will be transported to the shielded facilities for treatment and vitrification testing.

The treated waste is transported to the shielded cells facility of the SRTC. At the SRTC, the following technologies will be tested:

- A computer model will be used to determine the appropriate amounts of frit and trim chemicals to be added prior to vitrification.
- The resins and sorbants will be vitrified in a joule-heated melter.
- The offgas from the melter will be monitored in a series of filters, traps, and bubblers that will be sampled to assure that the emissions of hazardous material are well below regulatory levels.
- The durability of the final vitreous waste form will be determined using a Product Consistency Test (i.e., a standard high-temperature leach test that measures the durability of high-level vitreous waste forms).

In FY96, the scope of the project will be to:

- Arrange for shipment of samples from Oak Ridge Site to ANL and SRTC
- Obtain acceptance for disposal of the final waste form
- Demonstrate treatment of cesium-loaded separation media on a laboratory scale at ANL

In FY97, the hot cell facilities at these sites will be prepared for demonstrations using actual wastes. In FY98, the scope of the project will be to vitrify cesium from the cesium-loaded separation media at SRTC and document the results of the resin treatment and vitrification studies.

## **BENEFITS**

Vitrification has been selected for further testing, because it is an established technology that offers the following benefits over the other options:

- Less expensive than other technologies available
- Offers a large volume reduction
- Produces a waste form that is very durable
- Can be used for a wide variety of waste streams

The cesium-loaded separation media must be treated prior to vitrification so that the media become solutions or slurries that can be fed to the melter. Treatment prior to vitrification will also improve the waste form quality and increase the loading of waste in the final waste form. A higher waste loading will minimize the amount of HLW that will need to be transported to a permanent geologic repository.

## **COLLABORATION/TECHNOLOGY TRANSFER**

A number of national laboratories and private industry are collaborating to achieve successful technology demonstration. ORNL is designing, constructing, and operating the mobile system for removing cesium from highly-radioactive waste. ANL is developing a process for treating the waste prior to vitrification.

Most of the technologies that will be used to safely solidify the waste material are based on work that has been completed at SRS. Prior development work that will be used for this project includes:

- The resorcinol-formaldehyde resin for removing cesium from HLW supernates
- The model for determining the optimum amount of frit and chemicals to add to the waste prior to vitrification
- The code for predicting key characteristics of vitreous waste forms based on free energies of hydration
- The joule-heated melter located in the SRTC shielded cells facility
- The Product Consistency Test

The Office of Environmental Management is sponsoring these projects. The results will be transferred to other DOE sites, private industry, and any other interested parties, as appropriate, through reports and conferences.

### **ACCOMPLISHMENTS**

- Final design drawings completed for the CsRD system will be used to remove most of the radioactivity from 25,000 gallons of Melton Valley Storage Tank supernate.
- ORNL and SRS representatives met with providers of radioactive material transportation services so that, after the CsRD system begins to operate, the waste can be provided to ANL.
- Radiation dose rates associated with resin and final waste form have been predicted; shielding options for the SRTC shielded cells facility are being discussed.

### **TTP INFORMATION**

Vitrification of Ion Exchange Resins technology development activities are funded under the following technical task plan (TTP):

TTP No. SR16WT31, "WSRC Immobilization"

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### **BIBLIOGRAPHY OF KEY PUBLICATIONS**

None available at this time.

## 5.0

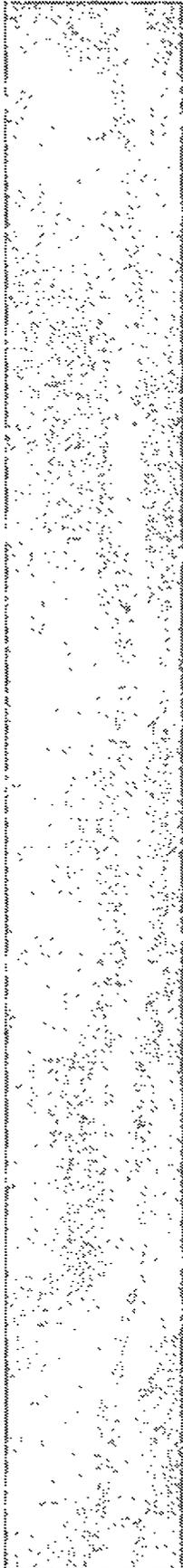
# CROSSCUTTING PROGRAMS

EM-50 has three crosscutting programs: Efficient Separations and Processing (referred to as Efficient Separations or ESP); Characterization, Monitoring, and Sensor Technology (referred to as Characterization or CMST); and Robotics Technology Development (referred to as Robotics or RTDP). Each of these programs has technology development activities that overlap the boundaries of the individual focus areas. The focus areas and the Crosscutting Programs share the view that knowledge and understanding of the needs of the focus areas are critical for mutual success. Hence, the focus areas and Crosscutting Programs strive to develop and maintain effective communications with the Site Technology Coordination Groups as well as among themselves.

Crosscutting Program activities focus on technologies that have multiple applications within the focus areas so that development efforts and costs are not duplicated among focus areas. This results in a development cycle in which a Crosscutting Program will develop and demonstrate a basic technology that can be transferred to a focus area to address its individual needs. In other cases, the technology will be directly applicable without additional development effort.

The Efficient Separations Crosscutting Program was created to identify, develop, and perfect technologies and processes to treat wastes and address environmental problems throughout the DOE complex. Initially ESP technology development efforts focused on the treatment of high-level waste from the underground storage tanks because of the potential for large reductions in disposal costs and hazards. Treating wastes requires separation methods that concentrate contaminants or purify waste streams for release to the environment or for downgrading to a waste form less difficult and expensive to dispose of. The mission of the ESP Crosscutting Program is to provide separations technologies to process, concentrate, and immobilize wastes. Examples of technology development activities that support the Tank Focus Area (TFA) include the following:

- Development and testing of several compounds (including crystalline silicotitanate, pillared clays, and potassium cobalt hexacyanoferrate) designed to extract radionuclides such as cesium and strontium from tank waste
- Development of sorbents for extraction of technetium and actinides from liquid wastes
- Development of supernatant pretreatment and processing systems



The Characterization Crosscutting Program develops characterization, monitoring, and sensor technology to effect cleanup and ensure worker safety. All the focus areas have characterization, monitoring, and sensor development needs. Therefore, technologies developed for one focus area can often be adapted to solve the problems in another. The CMST Crosscutting Program identifies technology gaps between baseline technologies and focus area needs, integrates technology development, and leverages resources to achieve synergies in development and to provide cost-effective solutions. The CMST Crosscutting Program supports the TFA by developing safe, fast, economical methods and instruments for characterizing and monitoring the gaseous, liquid, and solid contents of high-level waste tanks to address safety questions, and for assuring safety during storage, retrieval, processing, and disposal. The primary CMST strategy is to develop sensors for deployment in the tanks for in situ, real time, measurement. Examples of CMST technology development activities that focus on tank remediation include the following:

- Development of a field-portable, fiber optic Raman spectrograph that can be used to obtain chemical fingerprints of hazardous wastes in the storage tanks of concentrated and dilute environmental contaminants
- Development of an in situ viscosity and density monitoring system to help optimize sluicing operations at tank sites; measurement of tank volumes and transport lines minimizes water additions needed to effectively pump waste and avoid pump or line plugging
- Development of a small nonmechanical sensor for measuring viscosity and shear strength of tank waste slurries
- Development of an interactive computer-enhanced remote viewing system that can provide a reliable geometric description of a work space in a fashion that will enable robotic remediation tasks to be carried out more effectively and economically
- Development of two acoustic monitoring instruments to indicate if the sludge and supernatant components within the tank are completely mixed
- Development of a robotic tank inspection end effector capable of both visual and nondestructive evaluation of the interior wall of stainless steel and carbon steel waste storage tanks

The Robotics Crosscutting Program is critical to the operational success of waste tank remediation. Due to high radiation, harmful chemicals, massive waste loads, and restricted entry ways, tanks are inaccessible for human labor. Robotics systems are safe, efficient, and cost-effective means to automate the many characterization and retrieval operations associated with tank remediation. RTDP develops deployment arms, manipulators, and associated control systems to enable remote characterization, sampling, and retrieval of tank waste; to inspect and monitor the tank structure; and to observe in situ

operations. Some development activities underway within the Robotics Crosscutting Program that support the TFA include the following:

- A manipulator end effector capable of measuring residual contamination on tank walls and floors has been developed. This end effector will be deployed before, during, and after waste retrieval operations to locate and measure residual contamination sources.
- In FY97, Oak Ridge National Laboratories will begin removing radioactive waste from a large underground Gunitite tank using the Modified Light Duty Utility Arm (MLDUA). Control system enhancements are needed to reduce vibrations induced by motion of the MLDUA and dynamic effects induced by the waste dislodging and conveyance end effector.
- In FY96, advanced flexure control software will be developed for the MLDUA. Extensive simulation testing will be used to verify that the software is optimized for the MLDUA. In FY96, the software will be integrated into the MLDUA control system.

For more information on the Crosscutting Programs, please see the 1996 Technology Summary Books for the Efficient Separations and Processing Crosscutting Program; the Characterization, Sensor, and Monitoring Crosscutting Program; and the Robotics Technology Development Crosscutting Program.

## 6.0

# SITE SPECIFIC TECHNOLOGY DEVELOPMENT ACTIVITIES

The mission of the Tank Focus Area (TFA) is to establish an efficient link between technology development and the final users of improved technology systems. TFA's mission also includes improving coordination between technology development activities. In addition to the Office of Science and Technology (OST), development of technologies to make tank remediation safer and more cost effective has been done by a variety of organizations, including:

- The Tank Waste Remediation Systems (TWRS) at Hanford
- The Office of Waste Management (EM-30) at the Idaho National Engineering Laboratory (INEL)
- The Office of High Level Waste Management (EM-30) and the Savannah River Technology Center (SRTC)
- The Office of Environmental Restoration (EM-40) and the Office of Waste Management (EM-30) at the Oak Ridge National Laboratory (ORNL)

Technology development by these organizations has, by design, been more site specific than that of OST. Nevertheless, DOE recognizes that sites may have common needs which enhance the ability to leverage off one another. This coordination is one function of the TFA.

This section of the Technology Summary book contains short descriptions of some of the technology development initiatives by the organizations listed above.

## 6.1

## HANFORD

### THE HANFORD TANK INITIATIVE

The TFA and the Hanford TWRS are collaborating on a major initiative to prepare one or more tanks at Hanford for closure, bringing innovative technology and processes to bear to address this problem. Key objectives of the project will be to enlist early involvement of regulators and stakeholders in defining closure requirements, and then to expedite the closure of one or more single shell tanks (SSTs) at Hanford. In situ characterization technologies and technologies needed for retrieval of waste from a potentially leaking tank will be high priorities for this full-scale demonstration activity. This activity is being planned and coordinated in FY96 with demonstration operations expected to be initiated during FY97.

### HANFORD - SAFETY

**Flammable Gas Generation.** The release of flammable gases into the dome space of Tank 101-SY and other waste tanks at the Hanford Site has been a top priority safety issue. Periodic releases can result in concentrations of flammable gases in the dome space above lower flammability limits (LFLs). A mixer pump was installed in 101-SY to test its efficacy as a mitigation measure in preventing periodic releases of hydrogen. This approach has been reasonably successful and work is currently focused on modeling and designing similar mitigation systems for Tanks 103-SY, 101-AW, 103-AN, and 104-AN. Specific activities include:

- Developing and deploying void meters and viscometers in each tank to characterize key waste properties
- Performing modeling of gas generation mechanisms and gas release mechanisms in both double shell tanks (DSTs) and SSTs to support safety analyses and evaluate mixer pump performance
- Performing gas retention testing on actual waste
- Modeling flammability and detonation to understand the effects of gas concentration and tank geometry on the flammability of gas mixtures above the waste

## **FERROCYANIDES AND ORGANICS IN TANKS SAFETY ISSUES**

Ferrocyanides were used in past operations to precipitate fission products out of the high-level waste (HLW) in tanks. The ferrocyanide residues left in the tank waste pose a risk of exothermic chemical reactions if the wastes are allowed to dry out and self-heat. Previous work in this area has indicated that it is likely that much of the ferrocyanide in the tanks has been chemically broken down over the years and is no longer present in significant enough quantities to cause concern. Work planned for this year will be to conduct additional aging studies on both simulated and actual wastes to determine whether the assumptions about ferrocyanide degradation can be confirmed.

The organic safety issue results from organic complexants and organic degradation products of solvents that have been added to the SSTs as a result of Hanford operations. These waste tanks may also contain enough sodium nitrite and sodium nitrate oxidizers to exothermically oxidize the organic compounds. Analyses show that these reactions could occur if there is sufficient concentration of fuel and oxidizer present in the waste, and if a portion of the waste is dried out and heated to temperatures above 180°C. DSTs containing organics are not considered a safety issue because the tanks contain large quantities of water. Water has been removed from SSTs due to the risk of leakage. This project is analyzing the risk from the Organic Safety Issue by studying several areas:

- Waste aging and the degradation of fuel value of the organics due to radiolysis or chemical decomposition
- The energetics of potential reaction systems within the tank
- Using advanced methods such as the Light Duty Utility Arm (LDUA) with a moisture detection end effector to determine in situ whether conditions in a tank are safe

## **HANFORD - CHARACTERIZATION**

In FY95, the TFA and the Hanford TWRS jointly kicked off an accelerated effort to deploy Advanced Hot Cell Analytical Technology (AHCAT) for the rapid analysis of tank waste core samples in a hot cell. Development activities include:

- Scanning analysis of gamma and high-energy beta emitting radionuclides in core samples
- Laser ablation mass spectroscopy for rapid elemental analysis of core samples

- Raman probe for molecular analysis of key constituents
- Near infrared (NIR) spectroscopy for moisture analysis
- Thermogravimetric offgas analysis
- Organic complexant analysis
- Inductively coupled plasma/mass spectroscopy

In addition, there are projects for the development of two techniques for use in situ. These are the neutron moisture probe for measuring near surface moisture content of the waste, and an in situ Raman/NIR probe for detecting organics in the waste, which are the subject of one of the safety issues noted in the previous section.

## **HANFORD - PRETREATMENT**

Pretreatment technology development at Hanford is done primarily in support of either the low-level waste (LLW) or HLW disposal programs. The need for this activity has been recast in FY96 due to DOE's decision to privatize the remediation of HLW in tanks. The first phase will address the supernatant waste which will be pretreated to produce LLW and interim storage of the HLW fraction. Additional information on privatization is provided in the following sections.

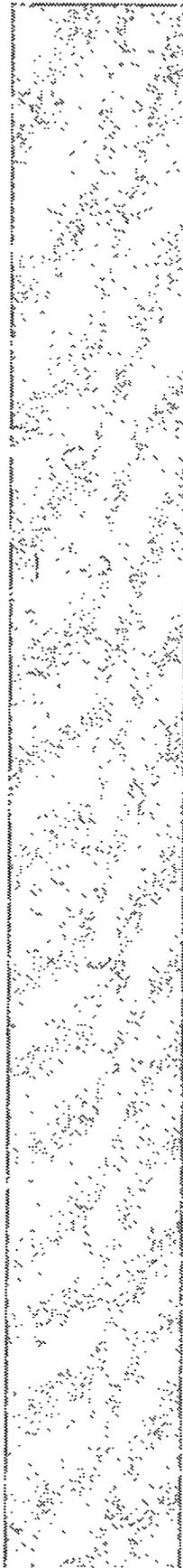
TWRS' primary need for technology development is now reduction of technical risk in the event that privatization is not successful, and for the preservation of core technology development skills necessary to evaluate privatization proposals. The pretreatment development activities planned for FY96 include the following:

- Sludge washing of HLW sludges to be processed in both Phase I and Phase II of privatization
- Technetium removal from supernatant
- Solid/liquid separation - settle/decant

Other pretreatment studies that will benefit Hanford are being performed by the Tank Focus Area and the Efficient Separations and Processing Crosscutting Program.

## **HANFORD - IMMOBILIZATION**

Technology development for the LLW disposal program is also part of the risk reduction approach to support privatization. Pretreatment and immobilization are the primary elements of Phase I of TWRS privatization. The main



objective of Phase I will be to demonstrate the LLW treatment technology on a large scale, and the vendors selected will be expected to bring as much existing technology to the table as possible or develop it themselves.

As part of the risk reduction program, the following projects are planned for LLW technology development in FY96:

- Compile a database of melter performance test results from previous LLW vitrification demonstration contracts
- Conduct modeling and tests to predict long term release of contaminants from a glass LLW form
- Conduct a field experiment to measure actual release of contaminants from glass and transport of contaminants through typical Hanford soil
- Conduct a study to identify materials which could scavenge contaminants from the waste if placed near the disposal site
- Develop new waste form durability testing methods that will be applicable to measuring performance of LLW at Hanford
- Develop techniques for inspection and acceptance of LLW form product to allow verification of performance with specifications
- Carry out hot vitrification crucible tests to evaluate LLW glass formulations with actual waste from Tank 101-AW

Technology development for the HLW program is also planned under the TWRS program in FY96. Plans for implementation of this technology would be much longer term than those for LLW since HLW treatment is not addressed until Phase II of privatization is initiated. Processing of HLW in Phase II is expected to begin by 2009. Technology development projects planned for FY96 include:

- Conduct radioactive vitrification testing of HLW sludges (to be optionally included on Phase I privatization)
- Develop a process for immobilization of a technetium-rich waste stream
- Optimize waste loading for HLW and develop a high waste oxide loading formulation
- Use simulants and a small scale HLW melter system to test processing characteristics, product properties, materials of construction, waste oxide loading, and other parameters
- Develop waste inspection and acceptance techniques to allow measurement of the waste form performance relative to specifications

## **HANFORD - RETRIEVAL AND CLOSURE**

Under the current plans for remediation of HLW in tanks at Hanford, the retrieval function will continue to be the responsibility of the site management contractor, and closure to meet technical and regulatory requirements will be a closely related function. Technology development will be needed to provide a basis for closure criteria as well as advanced technologies for retrieval of the waste with minimal impact to the environment and downstream processing of the waste. Technology development activities for FY96 that relate to this work include:

- Scanning of industry [by the Acquired Commercial Technology for Retrieval (ACTR) project] for available technology or related technology that can be adapted toward the TWRS to avoid unnecessary development
- Performing a trade-off study of tank leak detection and mitigation systems needed to support sluicing of waste from potentially leaking SSTs
- Developing a regulatory strategy and dialogue regarding the requirements for tank closure that will drive the technical needs for the program
- Evaluating advanced design mixer pumps for the mobilization of solids from wastes in DSTs

## **HANFORD - STORAGE AND DISPOSAL**

A few projects related to the performance of an LLW waste form, transport of contaminants through soil, and assessment of possible impacts to soil and groundwater from the disposal site are included with the LLW disposal program during FY96 and were described in previous sections.

## IDAHO - SAFETY

**Systems Analysis Support.** The state of Idaho requires that DOE cease use of some of its SSTs in 2009 and the remaining tanks in 2015. Additionally, a Settlement Agreement with the state requires that DOE complete calcination of sodium-bearing liquid high level wastes by December 31, 2012. Current operating facilities, as configured, cannot process the liquid wastes in the existing tank farm in time to comply with the Settlement Agreement. The current calcination process must be modified, or a new process and production facility must be constructed to remove the wastes from the tanks and condition the waste for disposal. The DOE Idaho Operations Office has directed Lockheed Idaho Technology Company (LITCO) to find and implement the most efficient and cost effective method for processing the HLW and sodium bearing waste inventory, and to cease use of the current Idaho Chemical Processing Plant (ICPP) tank farm.

Current analysis efforts have evaluated the 1) management options available to ICPP waste operations, 2) sodium-bearing liquid waste treatment technology alternatives, 3) calcine waste treatment technology alternatives, 4) high activity immobilization alternatives, and 5) low activity immobilization alternatives. Treatment alternatives have been identified, and planning of the technology development is in progress.

## IDAHO - RETRIEVAL

**INEL Light Duty Utility Arm.** This project supports development of Function and Requirements documents for, and provides plant review of, EM-50 development of end effectors for tank inspections. Researchers are designing and fabricating a camera system and sampler system for tank inspection and subsequent characterization. They are also designing and reviewing a nondestructive examination and effector, minilab characterization end effector (initial development provided by Sandia), and a gripper end effector. EM-30 will procure the INEL LDUA for application at the ICPP tank farm for inspection and subsequent characterization of the tanks. The arm will be used for inspection of tank walls to determine tank integrity, characterization of waste to develop tank integrity, and characterization of waste to develop waste simulants for testing and demonstrations. The project has completed hot demonstration of nondestructive examination end effectors for tank inspections, developed operating procedures and system operability tests, completed a tank condition assessment report, and developed a waste simulant.

**Decontamination Development.** LITCO has been developing various decontamination techniques that are designed either to help decontaminate an empty tank or to minimize the amount of liquid added to the ICPP tank farm. Some of the developed technologies include nonsodium liquid decontamination chemicals, strippable coatings, CO<sub>2</sub> blasting, grit blasting, nondestructive concrete decontamination, laser ablation, and other innovative techniques. Recently imposed funding constraints will limit future decontamination technology development.

## **IDAHO - PRETREATMENT**

**Calcine Retrieval, Pretreatment, and Dissolution Methods.** The purpose of this project is to develop and demonstrate equipment for retrieval, pretreatment, and dissolution of the calcine stored in Calcine Bin Set 1. Calcine retrieval has been demonstrated on 1/4 scale models, and the information gained may be used to support a Bin Set 1 calcine removal project pending completion of a safety analysis and a review of stress relief options. Calcine dissolution has been demonstrated on laboratory and bench scale using simulated calcine, and in a laboratory scale on actual hot calcine. Calcine blending/mixing has been demonstrated on a pilot plant scale. Researchers interface closely with separations and immobilization personnel to understand flow rates and product quality for the dissolution and pretreatment process.

## **IDAHO - IMMOBILIZATION**

**New ICPP Waste Mission Activities.** The purpose of this project is to develop waste formulations and specifications for immobilized waste forms from the HLW fraction of a separation process and for directly immobilizing ICPP wastes. It will develop criteria for the selection of immobilization equipment and it will demonstrate HLW immobilization. Expertise is leveraged by developing technologies to immobilize both liquid and calcine wastes with common equipment/processes. Researchers are also investigating HLW forms that meet permanent repository and waste acceptance criteria. The project works closely with separations personnel to understand feed compositions of the HLW immobilization process.

**LLW Stabilization Hot Lab Tests and Design and Build a Sodium/LLW Cold Pilot Plant.** The purpose of this project is to develop, through laboratory, pilot plant, and mock-up testing, an approved, cost-effective, optimized, and accepted immobilization form for LLW generated from the pretreatment and separations of existing HLW and future ICPP (Idaho) radioactive sodium wastes and calcines.

Cold laboratory tests with surrogate pretreated radioactive sodium waste have been completed with an emphasis placed on grout (cement) formulations. Glass and alternative forms are also being investigated. A conceptual design for the grout pilot plant has been completed. A Waste Acceptance Criteria draft document for an LLW disposal site is also in progress. A system analysis study has been completed which identifies cement grouting as the preferred option.



## 6.3

# SAVANNAH RIVER

### SAVANNAH RIVER SITE - SAFETY

***In-Tank Precipitation (ITP) Safety/Process Envelope.*** Investigation of the process phenomena for benzene generation during ITP facility operations will continue. The Savannah River Site (SRS) will identify necessary process or facility modifications. Key safety related process conditions, requirements, and limits for safe operation of the ITP facility will be established and incorporated into the Technical Safety Requirements. This work will provide a sound technical basis for updates to the ITP Addendum to the Tank Farm Safety Analysis Report.

***Defense Waste Processing Facility (DWPF) Safety/Process Envelope.*** The key safety related process conditions for operation of the Chemical Process Cell and the Late Wash Facility with radioactive precipitate feed from ITP will be defined and the necessary analyses performed to revise the DWPF Safety Analysis Report and Technical Safety Requirements to cover such operations.

***Manage Tank Waste.*** Many of Savannah River's HLW tanks are of ages at, close to, or in excess of their original design life. To ensure continued safe storage of wastes, appropriate metallurgical, equipment engineering, and process support work will be performed. Researchers will provide analysis and inspection techniques to assure the continued integrity of the tanks and process transfer systems.

***Waste Retrieval.*** A key element of the evaluation of various candidate technologies and approaches for retrieval of tank wastes will be careful consideration of potential safety concerns. This task will fully address the criticality, deflagration, or explosion potential for all candidate waste retrieval options. It will provide the analytical support to quantify hazard and risk and to revise safety analysis documentation as appropriate.

***Manage System Generated Waste.*** This program requires the safe handling, processing, and storage of waste generated from the DWPF process. Major tasks include collecting, treating, and discharging all radioactivity contaminated process waste from the HLW system; Packaging, characterizing, and shipping solid waste in a way that meets solid waste disposal acceptance criteria; collecting, treating, monitoring, and discharging gaseous effluents generated from HLW processing operations; collecting organic effluents, treating as required to meet disposal facility criteria; and storing for processing/disposal.

## SAVANNAH RIVER SITE - CHARACTERIZATION

**Develop and upgrade DWPF Analytical Methods.** This project is to deliver accurate and efficient analytical methods to meet DWPF requirements for process control and process history/diagnostics. Research tasks include any safety or downstream process concerns regarding organics in the DWPF recycle to the Tank Farms, and evaluating slurry sampling and dissolution techniques to reduce analytical time. Accurate analytical methods unique to waste vitrification are required to meet stringent quality controls imposed by Waste Compliance. Current chemical methods are time consuming and DWPF Laboratory capacity can potentially become a processing bottleneck.

## SAVANNAH RIVER SITE - RETRIEVAL

**Equipment Engineering Support.** This project is to provide equipment engineering support to ensure integrity of process transfer systems. Major tasks include developing improved techniques and equipment for salt sampling and salt mining, developing removal techniques for mining equipment, and developing riser probing techniques for pump installation.

**Waste Removal.** This project is to demonstrate technologies for removing waste (salt and sludge) from existing underground storage tanks for transfer to pretreatment facilities. Major tasks include determining salt dissolution kinetics, evaluating pump operation and installation requirements, developing methods to remove mixed salt and sludge, developing methods to remove dry/hardened sludge, and developing methods to remove tank heels. These efforts will support the initiative to close one storage tank within a year's time and up to four more storage tanks within two years' time. The Office of Science and Technology is supporting the development of tank closure criteria by providing the resources for analytical performance evaluations of various candidate tank closure methods.

## SAVANNAH RIVER SITE - PRETREATMENT

**In-Tank Precipitation.** This project treats salt solution to remove cesium by precipitation with sodium tetraphenylborate (STPB), and to remove soluble strontium, uranium, and plutonium by absorption on monosodium titanate. Major tasks include providing feed and hold tank pump operating strategy to reduce foaming and temperature buildup, demonstrate filter cleaning techniques, and support benzene abatement technology.

**Precipitate Washing.** Major tasks include developing hot cell techniques and evaluating samples to ensure the ITP process meets performance requirements, evaluating reduced inhibitor requirements for washed precipitate

storage to minimize nitrite addition, and defining pitting corrosion rates to find inhibitor requirements and tank life.

**Late Wash.** This project provides analytical and process support to the late wash design and startup testing. Major tasks include quantifying the effects of insoluble particles on late wash filtration, conducting filtration tests on the Experimental Lab Filter (ELF) (especially duplicating a cleaning cycle), developing a model of the dynamic backpulse systems used to clean filters, and designing on-line nitrite/benzene monitors for Late Wash.

**Sludge Washing.** This project is to provide analytical, metallurgical, equipment engineering and process development to ensure sludge washing meets DWPF and safety requirements.

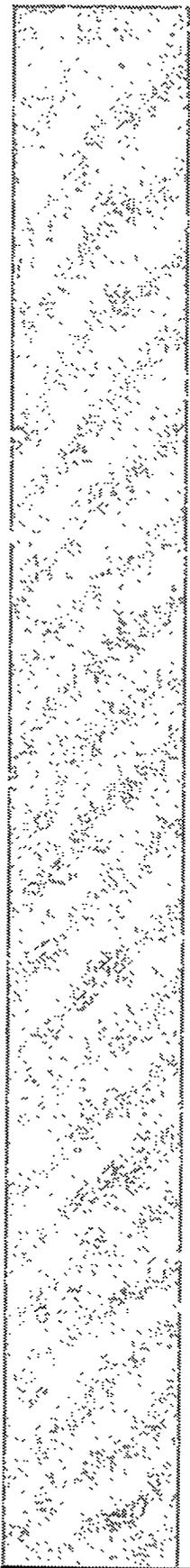
## SAVANNAH RIVER SITE - IMMOBILIZATION

**Glass Composition Formulation.** Researchers will develop predictive models, incorporate experimental data into the glass property models where there are insufficient data, and compare DWPF production glass properties with properties predicted theoretically. An important part of the work will be to assess projected waste feed compositions for both desired constituents and critical minor components with the greatest potential impact on waste loading and glass durability.

**Glass Sampling and Testing.** This project will show that the waste glass meets the Waste Acceptance Product Specifications. Major tasks include Product Consistency Testing; Scanning Electron Microscope and X-ray Diffraction analyses on glass grab and canister glass samples; determining the chemical composition and extent of crystallization of glass samples; and measuring the glass transition temperature, volatility, viscosity, and liquids of glass samples.

**Hydrolyze Tetraphenylborate (TPB).** This project provides a technique to remove organics (primarily benzene) from the precipitate slurry from Late Wash before transferring material to the Chemical Processing Cell. Major tasks include effectively implementing the SRTC technology and pilot-scale test experience to the field, conducting bench-scale runs, and developing a process for cleaning the Salt Process Cell vent.

**Prepare Melter Feed.** This project provides a method to blend and process the precipitate hydrolysis aqueous and washed sludge from the Tank Farm with frit. Major tasks include conducting bench-scale tests with simulants to model planned DWPF operation, defining DWPF recycle stream flows and compositions, determining nitroaromatic concentration in DWPF recycle streams, developing a reference process for cleaning the Chemical Process Cell vent, and addressing the method to dispose of cleaning solution(s).



**Saltstone Formulation and Disposal.** This project provides the technology to receive salt solutions from In-Tank Precipitation and effluent treatment operation. Major tasks include receiving dry feed materials, blending, and transferring to the premix feed bin; mixing salt solution and premix to produce grout; pumping grout to the disposal vaults; and backfilling around the vaults and capping with a layer of clean grout. Saltstone is pumped into large concrete disposal vaults where it cures. Capping the vaults with a layer of nonradioactive grout and backfilling the vault sides and top with soil will accomplish final disposal. Alternatives to the use of concrete vaults for saltstone disposal will be investigated to achieve cost savings without performance degradation. Support for this task will be provided as analytical performance evaluations of various candidate disposal techniques.

**OAK RIDGE NATIONAL LABORATORY - RETRIEVAL**

**Bulk Sludge Mobilization & Slurry Transport: Enhanced Submerged Jet Sludge Mobilization & Transport Studies.** The purpose of this project is to develop methods to mix and mobilize sludge in ORNL horizontal underground storage tanks, conduct slurry transport studies to design pipeline transport systems for ORNL liquid low-level waste (LLLW) sludge, and evaluate industrially available in-line solids monitoring instrumentation for ORNL LLLW sludge.

Mixing/mobilization studies have been initiated for enhanced submerged jet mobilization systems in 1/6-scale and 2/3-scale horizontal storage tanks using a simulated chemical sludge and Kaolin clay, a physical sludge simulant. Other advanced technologies such as pulsed jets and pulsed air are being considered. Slurry transport studies are also being initiated with ORNL and Hanford simulants to obtain design and operating conditions for slurry pipeline transport systems. The system is being modified to obtain minimum settling velocity data, and to test in-line solids monitors for pipeline transport of sludge.

This project is transitioning from a collaborative EM-30/40-funded activity to an EM-30/40/50 integrated, needs-based program at Oak Ridge and Idaho to mix horizontal tanks; and at Oak Ridge, Hanford, and the Savannah River Site for development of slurry transport. Investigators interact with other retrieval technology developers at ORNL and other DOE sites to leverage their retrieval efforts when possible.

**Modified Light Duty Utility Arm (MLDUA) System Development.** The Gunitite and Associated Tanks Treatability Study is one of the highest priority environmental restoration projects in Oak Ridge. The hazards associated with these tanks are sufficiently high so that the project is likely to continue at a high priority, yet sufficiently low so that cleanup progress can be made in the near term. This makes the activities at Oak Ridge an excellent proving ground for technology that could then be applied to the more challenging single-shell tank cleanup tasks at Hanford. This project is on an aggressive schedule with Federal Facility Agreement Milestones driving the project. A strong tie has been formed with EM-50 to leverage ongoing technology development activities.

ORNL is working with Westinghouse Hanford Company (WHC), INEL, Pacific Northwest National Laboratory (PNNL), Sandia National Laboratories, and Spar Aerospace Limited to design and build a modified version of the LDUA. The EM-50 Tanks Focus Area is developing the LDUA Program primarily for



deployment of characterization and inspection end effectors into the single-shell tanks at Hanford. INEL has also initiated procurement of an LDUA System for use in single-shell tanks. ORNL completed an initial Feasibility Study in June of 1994 that determined that a modified LDUA system could be developed to meet ORNL retrieval system requirements. ORNL has initiated a follow-on Feasibility Study with Spar to further detail the required modifications and anticipated cost for an MLDUA. To expand the mission of the LDUA to retrieval of Gunite tank waste, ORNL is modifying the LDUA. The modifications will increase the payload capacity, shorten and stiffen the vertical positioning mast, and alter the deployment system to allow deployment via a crane lift to a bridge support structure over the tanks, rather than truck-based deployment.

The bulk of the sludge in ORNL Gunite tanks was removed about 1983 using past practice sluicing. Removal of the heel requires a remotely operable system that can be deployed throughout the tank volume to mobilize the sludge and transport it to processing equipment at the surface. The LDUA and end effectors will be used to remove the residual sludge heel in the ORNL Gunite tanks. The modified LDUA will be of sufficient payload and reach to deploy both characterization tools and waste retrieval tools. Although the MLDUA cannot reach the entire tank volume of the largest tanks from a single access port, multiple ports can be installed and used by the MLDUA if this technology proves effective.

The MLDUA will be delivered to ORNL in approximately November 1996. Cold testing will be done through February 1997. Hot testing in the ORNL Gunite tanks will begin in March 1997 and continue throughout FY97. This will be the first arm-based, remotely operable waste retrieval system to be deployed in a large DOE underground waste tank. This is a collaborative EM-40/EM-50 project.

**Confined Sluicing Waste Retrieval End Effector System.** This project develops a high pressure water jet waste dislodging and conveyance end effector to remove sludge waste from the Gunite tanks. This end effector can be deployed both by a modified version of the LDUA, and by a smaller arm mounted on a mobile vehicle traveling in the tanks. This retrieval tool is being developed in cooperation with the EM-50 Tank Focus Area, PNNL, WHC, Quest, and the University of Missouri-Rolla. In parallel with this activity, a robotic vehicle that can be deployed without the aid of the LDUA will be tested.

This tool will be used to remove the residual sludge heel in the ORNL Gunite tanks. The bulk of sludge was removed about 1983 using past practice sluicing, and part of the remaining sludge is hard material that was not mobilized during the previous sluicing campaign. Therefore, a tool that can safely dislodge the remaining waste without damaging the tank is required. Removal of the heel requires a remotely operable system that can be deployed throughout the tank volume to mobilize the sludge and transport it to processing equipment at the

surface. The tests performed to date show that a variety of waste forms can be successfully mobilized and transported out of underground storage tanks using these water jet cutting techniques.

Procurement of field testable units was initiated in FY96. These units will be received at the end of FY96 and integrated with a deployment system at ORNL for cold testing. Cold testing will be completed by February 1997. Hot field testing will begin in FY97. This is a collaborative EM-40/50 project.

## OAK RIDGE NATIONAL LABORATORY - PRETREATMENT

**Cesium Removal Demonstration.** This collaborative EM-30/50-funded task will demonstrate the use of a skid-mounted mobile ion exchange system for processing contaminated high-salt content waste from ORNL underground storage tanks. The ion exchange system will use Ionsiv E-911, a crystalline silico-titanate sorbent developed by EM-50 and private sector collaboration. Crystalline silico-titanate was selected based on the results of FY96 sorbent comparison studies to remove radioactive cesium from 4-5M sodium nitrate. The demonstration will process up to 25,000 gallons of low level waste to meet Nevada Test Site or ORNL solid waste disposal facilities waste acceptance criteria. The loaded resins will be vitrified at Savannah River as a leveraged demonstration. The demonstration will determine processing capabilities, identify potential operating/maintenance problems for remotely operated mobile ion exchange systems, and show decontamination of the system for potential use at other sites. The project also considers issues such as worker health and safety, costs, disposal site waste acceptance criteria, and storage capacity limitations. The loaded ion exchange material will be used in an EM-50 vitrification demonstration.

Project scoping, planning, and preliminary system design will be completed in FY96. The demonstration will be primarily in FY97. After final demonstration, the unit will be transitioned to EM-30 for incorporation into baseline processing, or used to show separations capabilities of superior ion exchange materials being developed by the EM-50 Efficient Separations and Processing (ESP) Crosscutting Program.

**Out of Tank Evaporator Systems Demonstration.** This collaborative EM-30/50-funded task successfully demonstrated the use of a mobile, skid-mounted evaporator for processing 25,000 gallons of contaminated high-salt content waste from ORNL underground storage tanks in March 1996. The evaporator removed excess water for ORNL LLLW, a 4M sodium nitrate solution contaminated primarily with cesium and strontium. The demonstration concentrated the low-level waste by 25 percent and obtained decontamination factors over 5E06. A report is being written, and the system will be transferred to EM-30 for ongoing operation in FY96.

**Solids-Liquid Separations Demonstration.** This collaborative EM-40/50 project will demonstrate use of advanced solids/liquid separations equipment using actual waste retrieved from Gunite tanks during FY97. The equipment for this demonstration will be selected from the results of FY96 TFA comparison studies performed at SRS using simulants. Researchers interface with technology developers at ORNL, EM-40, EM-50 TFA, and other DOE sites to leverage as much as possible.

## OAK RIDGE NATIONAL LABORATORY - IMMOBILIZATION

**Sludge Immobilization Studies.** The purpose of this project is to perform cold and hot demonstrations to design equipment and set operating conditions and ranges for treatment of ORNL transuranic sludge for disposal at the Waste Isolation Pilot Plant (WIPP). This includes use of grout and vitrification to produce waste forms that meet WIPP and/or Nevada Test Site waste acceptance criteria. Pilot-scale demonstrations are planned for FY98 using actual waste retrieved from Gunite Tanks. Researchers interface with technology developers at ORNL, EM-30, EM-40, EM-50 TFA, ESP, and other DOE sites to leverage when possible with their immobilization technology development efforts.

# **DOE BUSINESS OPPORTUNITIES FOR TECHNOLOGY DEVELOPMENT**

## **WORKING WITH THE DOE OFFICE OF ENVIRONMENTAL MANAGEMENT**

The Office of Environmental Management (EM) provides a range of programs and services to assist private sector organizations and individuals interested in working with DOE in developing and applying environmental technologies. Vehicles such as research and development contracts, subcontracts, grants, and cooperative agreements enable EM and the private sector to work collaboratively. In FY95, 39 percent of Office of Science and Technology (OST) funding went to the private sector, universities and other federal agencies. EM's partnership with the private sector is working to expedite transfer of newly developed technology to EM restoration and waste management organizations, industry, and other federal agencies.

Several specific vehicles address institutional barriers to effective cooperation and collaboration between the private sector and DOE. These mechanisms include contracting and collaborative agreements, procurement provisions, licensing of technologies, consulting arrangements, reimbursable work for industry, and special consideration for small businesses.

## **INFORMATION ON EM**

The EM Center for Environmental Management Information provides the most current facts and documents related to the EM program. Through extensive referrals, the Center connects stakeholders to a complex-wide network of DOE Headquarters and Operations Office contacts.

To obtain information from the EM Center for Environmental Management Information, write or phone:

EM Center for Environmental Management Information  
U.S. Department of Energy  
P.O. Box 23769  
Washington, DC 20026-3769  
1-800-736-3282  
cemi@dgs.dgsys.com

## **THE COOPERATIVE RESEARCH AND DEVELOPMENT AGREEMENT**

The Cooperative Research and Development Agreement (CRADA) is a written agreement between one or more federal laboratories and one or more nonfederal parties through which the government provides personnel, facilities,

equipment, and other resources, with or without reimbursement, to support a shared research agenda. The nonfederal parties may also provide funds, personnel, services, facilities, equipment, intellectual property, or other resources to support the research. DOE developed a modular CRADA to be responsive to the needs of participants while protecting the interests of the government and its taxpayers. DOE also has issued the small business CRADA to expedite agreements with small businesses and other partners that meet DOE's requirements. During FY95, EM entered into more than 60 CRADAs.

### **THE RESEARCH OPPORTUNITY ANNOUNCEMENT**

The Research Opportunity Announcement (ROA) is a solicitation for industry and academia to submit proposals for potential contracts in basic and applied research, ranging from concept feasibility through proof-of-concept testing in the field. This mechanism is used when EM is looking for multiple solutions for a given problem. ROAs are issued annually by EM. The EM ROA provides multiple awards and is open all year. ROAs are announced in the *Commerce Business Daily*, and typically published in the *Federal Register*.

For questions on ROAs, contact:

Robert Bedick  
U.S. Department of Energy  
Morgantown Energy Technology Center  
P.O. Box 880, D01  
Morgantown, WV 26507  
(304) 285-4505

To learn about EM Technology business opportunities, connect to the METC Homepage:

<http://www.metc.doe.gov/business/solicita.html>

### **THE PROGRAM RESEARCH AND DEVELOPMENT ANNOUNCEMENT**

EM uses the Program Research and Development Announcement (PRDA) to solicit proposals from nonfederal parties for research and development in areas of interest to EM. The PRDA is used for projects that are in broadly defined areas of interest where a detailed work description might be premature. It is a tool to solicit a broad mix of applied research, development, demonstration, testing, and evaluation proposals.

For questions on PRDAs, contact:

Robert Bedick  
U.S. Department of Energy  
Morgantown Energy Technology Center  
P.O. Box 880, D01  
Morgantown, WV 26507  
(304) 285-4505

To learn about EM Technology business opportunities, connect to the METC Homepage:

<http://www.metc.doe.gov/business/solicita.html>

## **THE SMALL BUSINESS INNOVATION RESEARCH PROGRAM**

The Small Business Innovation Research (SBIR) Program promotes small business participation in government research and development programs. This legislatively mandated program is designed for implementation in three phases from feasibility studies through support for commercial application. DOE publishes solicitation announcements through the Small Business Innovation Research Office each year to define research and development areas of interest.

For further information about SBIR programs, contact:

SBIR Program Manager  
U.S. Department of Energy  
Small Business Innovation Research Program  
ER-33  
19901 Germantown Road  
Germantown, MD 20874-1290  
(301) 903-5707  
[sbir\\_sttr@mailgw.er.doe.gov](mailto:sbir_sttr@mailgw.er.doe.gov)

## **BUSINESS AGREEMENTS**

### **Cost-Shared Contracts**

Nonfederal parties working under DOE contract can agree to share some of the cost of developing a technology for a nonfederal market. This arrangement may involve cash, in-kind contributions, or both.

### **Grants and Cooperative Agreements**

These contractual arrangements provide the recipient with money and/or property to support or stimulate research in areas of interest to DOE. DOE regularly publishes notices concerning grant opportunities in the *Commerce Business Daily*.

### **Research and Development Contracts**

This acquisition instrument between the government and a contractor provides supplies and services to the government. DOE may enter directly into research and development contracts, and DOE laboratories and facilities can subcontract research and development work to the private sector. Announcements on requests for proposals are published in the *Commerce Business Daily* and are available through the EM Homepage on the Internet: [www.em.doe.gov](http://www.em.doe.gov)

### **Licensing Technologies**

DOE contractor-operated laboratories can license DOE/EM-developed technology and software. In situations where DOE retains ownership of a new technology, the Office of General Counsel serves as licensing agent. Licensing activities are conducted according to existing DOE intellectual property provisions and can be exclusive or nonexclusive, for a specific field of use, for a geographic area, United States or foreign usage. Information on licensing technologies may be obtained by contacting the Office of Research and Technology Applications (ORTA) representatives listed later in this section.

### **Technical Personnel Exchange Arrangements**

Personnel exchanges provide opportunities for federal or DOE laboratory scientists to work together with scientists from private industry on a mutual technical issue. Usually lasting one year or less, these arrangements foster the transfer of technical skills and knowledge. These arrangements require substantial cost-sharing by industry, but DOE has an advanced class patent agreement in place for this provision and the rights of any resulting patents become the property of the private industry participant. Contact an ORTA representative for more information.

### **Consulting Arrangements**

Consulting arrangements are formal, written agreements in which a DOE laboratory or facility employee may provide advice or information to a nonfederal party for the purpose of technology transfer, or a nonfederal party may consult with the laboratory or facility. Laboratory/facility employees participating in this exchange of technical expertise must sign a nondisclosure agreement. Contact an ORTA representative for more information.

### **Reimbursable Work for Industry**

This concept enables DOE personnel and laboratories to perform work for nonfederal partners when laboratories or facilities have expertise or equipment not available in the private sector. Reimbursable Work for Industry is usually termed "work for others." An advanced class patent waiver gives ownership of any inventions resulting from the research to the participating private sector company. Contact an ORTA representative for more information.



### **Office of Research and Technology Applications**

Each federal laboratory has an Office of Research and Technology Application. These offices serve as technology transfer agents for the federal laboratories. They coordinate technology transfer activities among laboratories, industry, and universities. ORTA offices license patents and foster communication between researchers and technology customers.

**ORTA Representatives:**

**Ames Laboratory**

Todd Zdorkowski  
(515) 294-5640

**Argonne National Laboratory**

Paul Eichemer  
(708) 252-9771/(800) 627-2596

**Brookhaven National  
Laboratory**

Margaret Bogosian  
(516) 344-7338

**Fermilab**

John Vernard  
(708) 840-2529

**Idaho National Engineering  
Laboratory**

Jack Simon  
(208) 526-4430

**Lawrence Berkeley National  
Laboratory**

Cheryl Fragiadakis  
(510) 486-7020

**Lawrence Livermore National  
Laboratory**

Rodney Keifer (510) 423-0155  
Allen Bennett (510) 423-3330

**Los Alamos National  
Laboratory**

Pete Lyons  
(505) 665-9090

**Morgantown Energy  
Technology Center**

Rodney Anderson  
(304) 285-4709

**National Renewable Energy  
Laboratory**

Mary Pomeroy  
(303) 275-3007

**Oak Ridge Institute of Science  
and Education**

Mary Loges  
(423) 576-3756

**Oak Ridge National Laboratory**

Bill Martin  
(423) 576-8368

**Pacific Northwest National  
Laboratory**

Marv Clement  
(509) 375-2789

**Pittsburgh Energy Technology  
Center**

Kay Downey  
(412) 892-6029

**Princeton Plasma Physics Laboratory**

Lew Meixler  
(609) 243-3009

**Sandia National Laboratories**

Warren Siemens  
(505) 271-7813

**Savannah River Technology Center**

Art Stethen  
(803) 652-1846

**Stanford Linear Accelerator Center**

Jim Simpson  
(415) 926-2213

**Westinghouse Hanford Company**

Dave Greenslade  
(509) 376-5601



## ACRONYMS

ACTR	Acquired Commercial Technology for Retrieval
AHCAT	Advance Hot Cell Analytical Technology
ANL	Argonne National Laboratory
ANS	American Nuclear Society
ARA	Applied Research Associates
CCD	Countercurrent Decanting
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CMPO	Octyl-(phenyl-N,N-diisobutyl carbamoyl) Methyl Phosphine Oxide
CMST	Characterization, Monitoring, and Sensor Technology Crosscutting Program
CPAC	Center for Process Analytical Chemistry at the University of Washington
CPT	Cone Penetrometer
CRADAs	Cooperative Research and Development Agreements
Cr (III)	Trivalent Chromium
Cr (VI)	Hexavalent Chromium
CsRD	Cesium Removal Demonstration
DOE-ID	Department of Energy, Idaho Operations Office
DSS	Double Shell Slurry
DSSF	Double Shell Slurry Feed
DST	Double-shell tank
DWPF	Defense Waste Processing Facility
ELF	Experimental Lab Filter
EM	Office of Environmental Management
EPA	Environmental Protection Agency
ERT	Electrical Resistance Tomography
ESP	Efficient Separations and Processing
ESW	Enhanced Sludge Washing

FFA	Federal Facility Agreement
FFC	Federal Facility Compliance (Act)
FTIR	Fourier Transform Infrared
GAAT-TS	Gunite and Associated Tanks - Treatability Study
GAATs	Gunite and Associated Tanks
HLW	High-level waste
HQ	Headquarters
ICP/MS	Inductively coupled plasma/mass spectrometer
ICPP	Idaho Chemical Processing Plant
INEL	Idaho National Engineering Laboratory
ITP	In-tank Precipitation
JIT ESP	Just In Time Extended Sludge Process
LA/MS	Laser ablation/mass spectroscopy
LDM	Leak detection/monitoring
LDUA	Light Duty Utility Arm
LFLs	Lower Flammability Limits
LITCO	Lockheed Idaho Technology Company
LLLW	Liquid Low-Level Waste
LLNL	Lawrence Livermore National Laboratory
LLW	Low-level waste
MCI	Megacuries
METC	Morgantown Energy Technology Center
MLDUA	Modified Light Duty Utility Arm
MS	Mass Spectrometer
MVSTs	Melton Valley Storage Tanks
NIR	Near Infrared
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
ORTA	Office of Research and Technology Application

OST	Office of Science and Technology
OTD	Office of Technology Development
PLS	Partial Least Squares
PNNL	Pacific Northwest National Laboratory
PRDA	Program Research and Development Announcement
PVC	Polyvinyl Chloride
RCRA	Resource Conservation and Recovery Act
R-F	Resorcinol-Formaldehyde
ROA	Research Opportunity Announcement
RPD	Retrieval Process Development
RTDP	Robotics Technology Development Crosscutting Program
SBIR	Small Business Innovation Research Program
SEM	Scanning Electron Microscope
SREX	Strontium Extraction
SRS	Savannah River Site
SRTC	Savannah River Technology Center
SST	Single-shell Tank
STPB	Sodium Tetrphenylborate
TFA	Tank Focus Area
TGA	Thermogravimetric Analysis
TPB	Tetrphenylborate
TRIC	Tank Riser Interface and Confinement
TRU	Transuranic
TRUEX	Transuranic Extraction
TTP	Technical Task Plan
TWRS	Tank Waste Remediation System
UST	Underground Storage Tank
WHC	Westinghouse Hanford Company
WIPP	Waste Isolation Pilot Plant