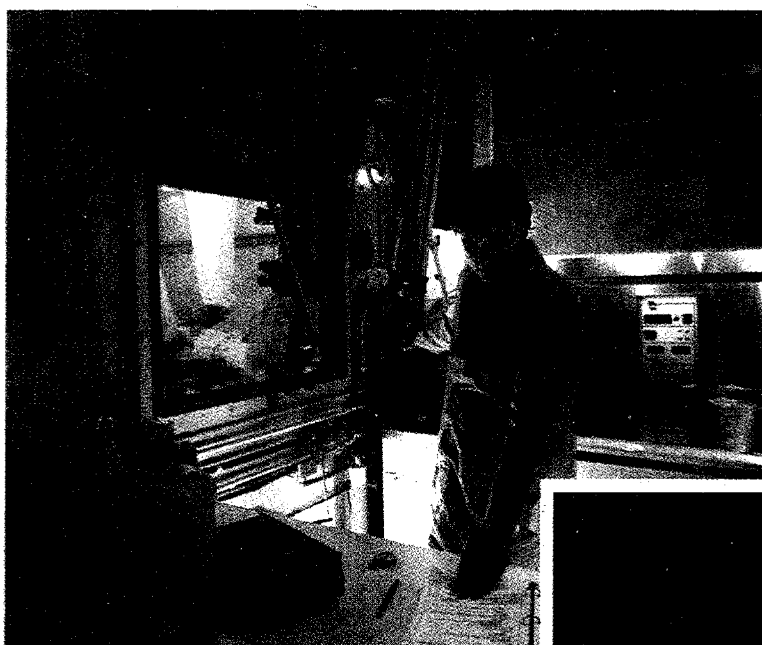
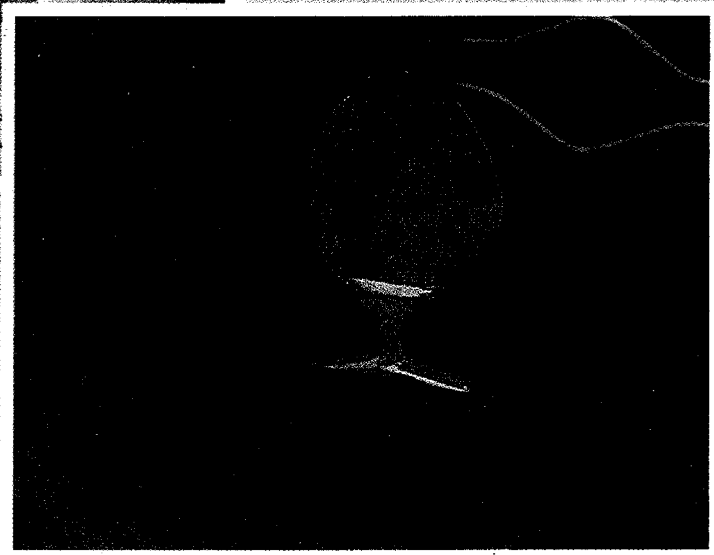
Characterization and Process Technology Capabilities for Hanford Tank Waste Disposal





Pacific Northwest National Laboratory
Richland, Washington

PNNL-10974

Characterization and Process Technology Capabilities for Hanford Tank Waste Disposal

J. L. Buelt
W. C. Weimer
R. E. Schrempf

March 1996

Pacific Northwest National Laboratory
Richland, Washington

Characterization and Process Technology Capabilities for Hanford Tank Waste Disposal

The purpose of this document is to describe the Pacific Northwest National Laboratory's (the Laboratory) capabilities in characterization and unit process and system testing that are available to support Hanford tank waste processing. The Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy (DOE). The Laboratory conducts research, development, and testing services in environmental restoration and waste management, environmental science, molecular science, energy, health and safety, and national security. The scientific and engineering capabilities of the Laboratory include physical, biological, chemical, environmental, materials, and computational sciences.

This document is organized into two parts. The first section discusses the Laboratory's extensive experience in solving the difficult problems associated with the characterization of Hanford tank wastes, vitrified radioactive wastes, and other very highly radioactive and/or heterogeneous materials. Several current and past programs conducted in or supported by the Analytical Chemistry Laboratory (ACL) are directly related to chemical characterization and analysis questions that will arise during the tank waste privatization efforts. Areas of expertise include chemical, radiochemical, and physical characterization; tank safety issues; pretreatment and disposal support; glass processing, analysis, and characterization; and quality assurance program development. The ACL is co-located with the Process Chemistry laboratories (used for radioactive process technology testing) in the 325 Building.

The second section of this document discusses the Laboratory's radioactive capabilities and facilities for separations and waste form preparation/testing that can be used to support Hanford tank waste processing design and operations. A significant trademark of the Laboratory's capability is its extensive radiochemical processing cells and laboratories and nonradioactive high bay laboratories and equipment. The Laboratory's expertise lies in development, scale-up, and deployment of first-of-a-kind processes to solve environmental problems, which includes extensive experience over the last two decades with high-level and low-level mixed tank wastes and their simulants. This part of the document focuses on the Laboratory's capabilities in thermal processing, separations, and radiochemical processing of radioactive tank wastes.

Characterization Technology Experience with Hanford Tank Wastes at the Pacific Northwest National Laboratory

Chemical, Radiochemical, and Physical Characterization

Those who take on disposal of tank wastes will only be successful with the support of an analytical laboratory able to deal with the complex waste materials. The ACL staff have been involved in tank waste characterization on the Hanford Site since the late 1980s and have experience in handling virtually all of the refractory tank waste types. Approximately one-half of the available extensive characterization data (physical properties, chemical composition, radionuclide composition, organic species) on tank waste composition has been developed within the ACL. The most highly radioactive samples and those containing high plutonium concentrations cannot be analyzed in other Hanford facilities; therefore, all samples from these tanks to date have been transferred to the ACL for analysis. In addition to the highly radioactive and high plutonium tanks, Laboratory staff have handled nearly all of the waste types in the Watch List tanks (i.e., gas generation tanks, ferrocyanide tanks, and organic tanks), as well as numerous single-shell tanks not on the Watch List. Laboratory staff also led the Tank Vapor Characterization Program, which characterized head space gas composition in more than 60 tanks.

Tank Safety

The Laboratory has been the principal provider of technical support in addressing issues relating to the safe storage of Hanford tank waste materials. These issues include flammable gas generation; hydrogen mitigation; ferrocyanide energetics, including waste aging; high organic tanks; high heat tanks; criticality safety; and vapor constituents and concentrations in tank headspaces. The Laboratory investigated the science that relates to waste properties and waste behavior in-tank and developed technologies to aid in characterization. The Laboratory's contributions include

- analytical characterization of real tank wastes for chemical, radiochemical, and physical properties
- laboratory investigations conducted with surrogate, simulant, and real waste
- tank waste data gathering and analysis
- engineering support for the development and deployment of waste tank instrumentation
- theoretical and modeling investigations of the chemistry and physics of tank waste materials.

Pretreatment and Disposal Program Support

Laboratory staff have improved process technology related to Hanford tank waste pretreatment and tank waste disposal activities. Research investigations have included the development of radionuclide-specific ion exchange resins, enhanced sludge washing abilities, investigations of safety aspects of both ferrocyanide and organic tanks, and waste form stability research. The Laboratory has been successful because we couple the process investigations and the requisite chemical analyses to provide information on the effectiveness of the various process steps. This analytical support, for both nonradioactive surrogate materials and actual tank wastes, has been provided by ACL staff.

The Analytical Chemistry Laboratory and Affiliated Pacific Northwest National Laboratory Chemistry Capabilities

For over 40 years, the ACL has been a full-service provider of analytical chemistry capabilities to the DOE, its contractors, and industrial clients. The ACL specializes in the analysis of highly radioactive materials and of very complex sample matrices. More recently this laboratory has provided analytical chemistry and engineering support to the development and operation of the Fast Flux Test Facility, a research breeder reactor that operated on the Hanford Site. During the past 7 years, the ACL has devoted a growing portion of its resources to supporting the Hanford Tank Characterization Program and other site remediation activities. Throughout its operational history, the ACL has also provided analytical chemistry services to a broad range of research and development programs at the Laboratory, the Westinghouse Hanford Company, and other Hanford Site contractors.

Analytical Chemistry Laboratory Staff

Approximately 75% of the technical staff in the ACL hold bachelors degrees, and more than one-third hold masters or doctorate degrees. The education and experience levels of these staff help assure a maximum value to clients. The analytical capabilities of the ACL are supplemented by chemistry staff and equipment, giving clients access to a broad spectrum of capabilities. Within the ACL, degreed staff members participate directly in the performance of analytical activities and operation of analytical instrumentation, and take direct ownership of instrument maintenance activities. This direct involvement of senior staff members ensures the highest reliability of instrument systems and the generation of the highest quality data.

The Laboratory's chemistry personnel have over 10 years experience in analyzing glass feed solutions and vitrification products. The ACL hot cell facility, the Shielded Analytical Laboratory, provided process chemistry support for producing 33 canisters of high-level waste glass for the German government. The ACL Inorganic Analysis Group has provided analytical support for numerous glass processing activities such as the Material Characterization Center's (MCC) simulated reference glass program, the High-Level Waste Vitrification project, and West Valley Nuclear Site vitrification activities. The ACL has been a participant in the six MCC round robins, which required dissolution and analysis of radioactive simulated glasses typical of vitrification processes for high-level nuclear waste.

Operations Management Systems to Support Characterization of Hazardous and Radioactive Constituents

The ACL has developed and applied an integrated operations management system that provides excellent visibility and control for all efforts in the laboratory. These systems ensure that all project requirements are met on time, within budget, and to the specified level of quality. The elements of this system enable real time prioritization of work, monitoring of technical progress, and detailed tracking of costs.

Starting with initial client contact, a project manager is designated as the single point of contact, with responsibility and authority derived from the ACL manager's office. This staff member represents a client advocacy and accountability role, and manages all work for that client. To the extent required, status reports, cost tracking and analysis, technical and quality reports, and presentations are provided.

A series of management systems generate the information used in tracking work from inception to close-out (see Figure 1). The ACL employs a Laboratory Information Management System that provides traceability and status of work. Weekly status meetings are the forum to discuss progress, issues, and priorities. The Laboratory's financial system provides timely budgetary and funding data to ensure effective control. If appropriate, rigorous project control criteria are applied to further enable detailed performance assessment. Finally, all records are centrally stored and sample analysis reports issued from a single control point within the ACL. These systems provide a collective capability, developed over several years, that ensures the mechanics of conducting the operations management functions are flexible and efficient.

The ACL continues to be in full compliance with all applicable quality, environmental safety and health, radiological control, and waste management regulations and Laboratory implementing systems and procedures. Furthermore, located within the 325 Building are two permitted treatment, storage, and disposal facilities that handle radioactive wastes and hazardous wastes on a daily basis. ACL staff, thus, have extensive experience interacting with federal and state regulatory agencies on a variety of issues.

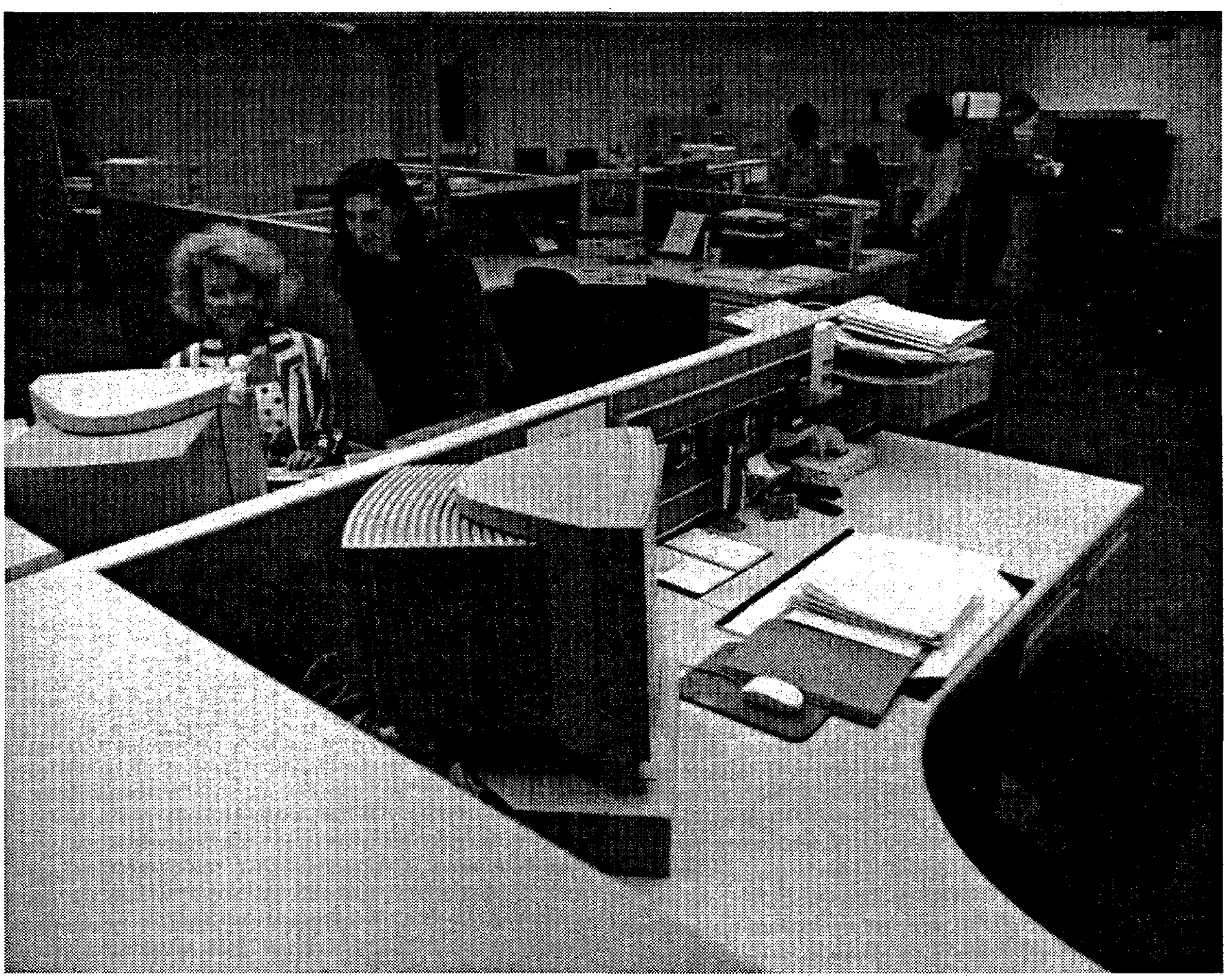


Figure 1. ACL Laboratory Support Office.

Quality Assurance Support

The quality assurance function within the ACL plays a key role in defining, in conjunction with the client, the data quality requirements for projects. Part of this role involves ensuring that the data quality strategy selected will pass regulatory scrutiny, while maintaining cost effectiveness and meeting schedule constraints. This function can also assist clients in the development of appropriate data assessment or validation strategies. This function has had significant involvement in determining the direction of the quality assurance program across the Hanford Site. The ACL was one of two principal developers of the Sample Exchange Evaluation Program, a Site comparison program for the analysis of radioactive tank waste materials. In addition, the ACL quality assurance function was a co-developer of the Hanford Analytical Services Quality Assurance Program, the Sitewide analytical quality assurance/quality control program. Also included within this function is a full-spectrum Standards Laboratory, which procures, prepares, and maintains records associated with standard materials for use on projects inside and outside the ACL.

Facilities for Handling Radioactive Samples and Materials

The Laboratory has several hot cell facilities that are available for performing work with highly radioactive Hanford tank materials. These facilities are located in several buildings in the Hanford 300 Area. Two of these facilities, located within the 325 Building, are particularly important to serving the needs of tank disposal because they are used for chemical process development and chemical analysis activities with highly radioactive tank materials.

The High-Level Radiochemistry Facility (HLRF) consists of three hot cells, totaling 180 sq. ft. of floor space, which are designed for conducting bench-scale and small pilot-plant scale process chemistry investigations with real waste materials. These cells have large front and rear galleries, very heavy shielding, high ceilings, and large access ports for transfer of samples and equipment. Bridge crane capacity can handle casks up to 30 tons. In addition, these cells contain some specialized characterization equipment for physical property determinations. The characterization capabilities within these hot cells are also duplicated outside of the hot cells in gloveboxes for less radioactive samples.

Located within the same building as the HLRF, the Shielded Analytical Laboratory (SAL), consisting of six cells that total 200 sq. ft. of floor space, is specially designed for performance of a variety of analytical chemistry operations within a cell on radioactive samples with dose rates of up to 2000 R/hr (see Figure 2). Cell size, shielding, access, viewing, and manipulators were selected to provide optimum cell design for performing remote chemical activities. Preparatory chemistry operations (dissolution, extraction, leaching, distillation, ion exchange, digestion, fusion) are performed on samples that are too highly radioactive to process in a fume hood or glovebox. Radioactive tank materials are prepared in these cells for further analytical or physical characterization processes. Specialized analytical instrumentation located within these cells or immediately adjacent to these cells permits selected sample analyses to be completed without transfer of the sample materials from the SAL hot cells to other analytical chemistry laboratories. For those analyses that must be completed in other laboratories within the 325 Building, "Lazy Susan" turrets on the rear face of the cells provide for rapid sample transfer out of the cells.

The HLRF and SAL work in tandem in the performance of many Hanford tank activities. Their proximity allows for very efficient operation; all sample receipt, experimentation, and analysis activities are conducted within one building, eliminating the need for multiple shipments of radioactive samples.

Measurement Capabilities for Chemical, Radiochemical, and Physical Characterization

Although the primary provider of radioactive analytical services is the ACL, the Pacific Northwest National Laboratory provides an integrated analytical characterization capability that is available to support the tank waste treatment activities.

Expertise from across the Laboratory can be applied to solve a wide range of analytical problems. These capabilities are a combination of

- unique facilities for the handling and processing of highly radioactive materials
- specialized analytical instrumentation, some of it designed specifically for analysis of highly radioactive samples
- staff who are experienced with the handling of highly radioactive materials and the analysis of highly radioactive samples.

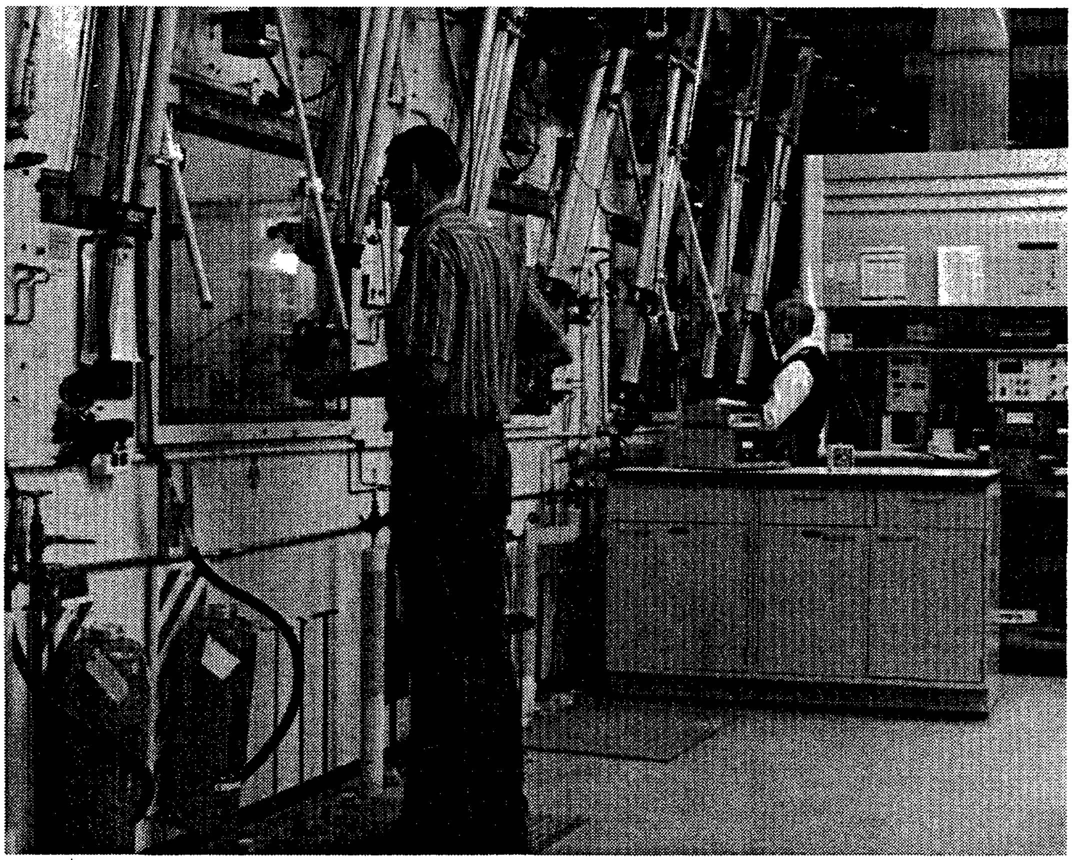


Figure 2. Shielded Analytical Laboratory.

This combination can provide waste analysis and characterization support to the tank remediation effort.

Analytical Instrumentation with Special Containment Features—For Analysis of Highly Radioactive Samples or Samples Containing High Levels of Alpha Activity

The Laboratory has developed several analytical instrument systems that are designed specifically for the analysis of highly radioactive samples or samples that contain elevated levels of alpha activity. These systems all employ some type of secondary containment for the analytical instrument. These systems have been developed to increase the overall efficiency of making particular analytical measurements. This efficiency is realized both in terms of a shortened analytical time and in terms of reduced "hands-on" time by analytical staff, thereby also addressing issues of occupational radiation exposure. All of this instrumentation is available to support tank activities, and most has been used routinely during the analysis of Hanford tank waste materials. Two recent acquisitions, which are currently in deployment, include a shielded, glovebox ICP-AES, directly attached to the SAL hot cells; and a glovebox ICP-MS.

The shielded, glovebox ICP-AES provides quantitative elemental determination in the ppm-to-percentage levels for highly radioactive tank materials and glass feeds/products. The ICP-AES uses a charge injection device detection system and can effectively measure and quantify any element that is ionized by the plasma. The system is attached to the analytical hotcell and can perform analyses directly on sample dissolutions, generating doses up to 5 R/hr. Since sample dissolutions do not need to be diluted because of high exposure, this system provides the best sensitivity for trace impurities in highly radioactive materials, such as waste glasses produced from double-shell tank feeds.

The glovebox ICP-MS covers a mass range from 3 to 300 AMU and demonstrates typical detection limits at the 1- to 10- ppt level. The ICP-MS provides elemental and radionuclide information on radioactive liquids and solubilized solids, such as waste glasses and tank core materials. The glovebox ICP-MS is particularly useful for providing radionuclide information on waste materials containing high levels of transuranic elements. Other instruments that are housed within a secondary containment include:

- In-hot-cell Total Organic Carbon System
- In-hot-cell Viscometer
- In-hot-cell Gamma Ray Spectrometer
- Shielded, Automated Gamma Ray Spectrometer for High Radiation Samples
- Glovebox Viscometer
- Glovebox Thermogravimeter/Mass Spectrometer
- Glovebox Atomic Force Microscope.

Other Analytical Instrumentation Used for Characterization of Hazardous and Radioactive Constituents

State-of-the-Art Radiochemistry Analysis Capability

The Laboratory's radiochemistry staff, using state-of-the-art equipment and procedures, are capable of determining the activity of most radioisotopes of interest in a wide array of matrices and a large range of radioactivity levels. Typical sample matrices include highly radioactive Hanford waste tank samples, soil, and water; air and sewer building effluents; bioassay (e.g., blood, hair, urine); neutron-activated reactor components; spent reactor fuel; and mixed wastes (oils, organics, and acids).

Sample preparation procedures include microwave digestion, caustic fusion, acid leaching and dissolution, and a microwave muffle furnace. Preparations can be done in hot cells for highly radioactive samples. Chemical separation procedures are based on ion exchange, extraction chromatography, precipitation plating, solvent extraction, and/or distillation techniques. Radiochemical tracers or elemental carriers are generally used to determine chemical yields. Approved chemical separation procedures are currently in place for the analysis of ^{3}H, ^{14}C, ^{36}Cl, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{79}Se, ^{90}Sr, ^{93m}Nb, ^{93}Zr, ^{99}Tc, ^{126}Sn, ^{129}I, ^{210}Po, U and Pu isotopics, ^{231}Pa, and Pu, Am/Cm, and Np by alpha energy analysis.

Alpha, beta, and gamma activities are measured using a large array of counting equipment, including Ge gamma detectors (up to 100% efficiency); gas flow proportional counters with dual alpha/beta capability; alpha energy analysis systems; liquid scintillation counters, two with dual alpha/beta spectral analysis; and ZnS alpha detectors. The counting systems are computer controlled with highly efficient data analysis and quality control software. Uranium can be measured at ppt (10^{-12}) levels using laser fluorimetry and kinetic phosphorimetry. Uranium and plutonium isotopes are measured with high precision using Thermal Ionization Mass Spectrometry. Many long-lived radioisotopes (of concern for long-term waste disposal) are measured by ICP-MS.

State-of-the-Art Inorganic Analysis Instrumentation

In addition to the two contained ICP systems described above, our inorganic analysis staff have available a full range of additional inorganic analytical instrumentation. This includes an ICP-AES (enclosed in a radiological fume hood) with 50+ channels covering the analytes typically found in Hanford process and waste materials. Typical applications for this system include the measurement of major, minor, and trace level concentrations of elemental analytes in radioactive liquids, tank supernates, and solubilized tank sludges, slurries, and salt cakes; synthetic and waste glasses; and in situ vitrified soils.

The Laboratory's ion chromatographic gradient systems provide quantitative determination for both inorganic and organic ions from the ppb-to-percentage range. The system supports anion determination in tank waste supernates and leachates; anion/cation monitoring for process analysis, such as glass feeds; and ion speciation quantification.

Accurate and precise elemental analysis at the ppb/ppt level can be achieved by the Laboratory's two transverse Zeeman graphite furnace atomic absorption spectrometers. These systems have been most useful for providing tank characterization or glass analyses for analytes not typically measured by ICP-AES, such as cesium and rubidium. The systems are also used to provide accurate measurements for EPA highly toxic metals.

The Laboratory has a full range of total organic carbon (TOC) analysis capabilities, including "hot persulfate" method (hot cell and benchtop), furnace method (fume hood), and solution UV-catalyzed method (fume hood). The Laboratory has established the TOC analysis method standard (i.e., hot persulfate method) applicable to tank waste materials. TOC/TIC analysis can be performed on radioactive liquids and solids in the ppm-to-percentage range. The various methods have provided high quality

TOC measurement for tank material safety concerns (energetics) and pretreatment and vitrification (glass solubility).

Several additional types of inorganic analyses are available as well. The Laboratory has the capability to quantitatively determine total cyanide from the ppb-to-percentage level in tank supernates/liquids, sludges/sediments, salt cake, or processing feeds. Particle size, particle volume, and other parameters can be evaluated by the ACL's particle size imaging system. The particle size system typically measures particles from 0.5 to 150 microns, with larger ranges being available. Particle size and volume distribution are typically measured to provide information about filtering requirements, blending processes, or pumping characteristics of slurries. The ACL uses numerous wet chemistry methods to provide valuable information for tank characterization and glass forming. Examples of such methods are chromium (VI) and silicate for tank characterization and pretreatment activities and iron(II)/iron(III) for glass feeds and products.

State-of-the-Art Organic Analysis Capability

The ACL's organic analysis staff are able to analyze routinely for known or regulatory-listed compounds at several levels of desired data quality (see Figure 3). The group has additional expertise and sophisticated instrumentation enabling the development of new methods for the analysis and/or identification of both known and unknown compounds. The ACL can analyze for volatile, semivolatile, nonvolatile, and thermally unstable organic compounds and complexes in many different sample matrices, including head space samples, sludges, tank wastes, soils, tissue, water, and oils.

Available analytical instrumentation includes sample introduction or extraction methods such as headspace, purge and trap, thermal desorption and extraction, and supercritical fluid extraction. Gas chromatographs are equipped with detectors that include mass spectrometers, Fourier transform infrared, atomic emission, nitrogen/phosphorus, and electron capture detectors. Liquid chromatographs

Figure 3. Organic Analysis Instrumentation Laboratory.

using electrospray and thermospray ionization are also employed for the mass spectrometry of nonvolatile samples.

Process Technology Capabilities at Pacific Northwest National Laboratory

Separations—Staff at the Pacific Northwest National Laboratory have developed much of the separations technology currently planned for application to cleanup of wastes in Hanford tanks. The Laboratory's expertise in a wide range of separations techniques solves major chemical processing challenges. These include phase transfer technologies (ion exchange, solvent extraction), membrane technologies (electrodialysis, reverse osmosis), supercritical fluids, and electrochemical technologies (electrochemical ion exchange, electrokinetics, electrochemical deposition, and electrochemical conversions).

Thermal Processing (Vitrification)—Vitrification technology experience and capability at the Laboratory includes low-level, transuranic, mixed, hazardous and nonhazardous solid wastes. With over 25 years of waste vitrification development experience, the Laboratory has the process and equipment knowledge to adapt vitrification to almost any relevant waste material. The Laboratory is responsible for the development and application of the joule-heated, slurry-fed ceramic melter, the baseline technology employed at the Defense Waste Processing Facility (DWPF) at the Savannah River Site and the West Valley Demonstration Project in West Valley, New York. The world's first remotely operated liquid-fed ceramic melter (LFCM) process was successfully designed, constructed, and operated by Laboratory staff. This process has been adopted in the United States, Germany, and Japan, where high-level waste treatment facilities have been constructed. With the development of this thermal processing technique, significant expertise and capability also has been developed with waste form development, testing, and qualification.

Radiochemical Processing—During the past decade the radiochemical capabilities at the Laboratory have concentrated on characterization and treatment of Hanford wastes. Necessary facilities and capabilities are available that include development and testing of separations processes, waste form formulation, conversion of waste to final waste forms, and evaluation of final waste form quality. The Laboratory's capabilities in radiochemical process engineering include development of process flowsheets and design, installation, and testing of radiochemical process systems including leaching, solvent extraction, ion exchange, vitrification, fuel dissolution, decontamination, evaporation, grouting, solid waste packaging and shipment, and high-level liquid waste shipping, receiving, and transportation. The radiochemical processing capability includes chemical engineering process development of toxic and highly radioactive systems. Representative foundation capabilities include separation, conversion, and process engineering augmented by remote systems technologies and hot cell operations (processing and characterization).

Separations

The Laboratory can provide a wide range of separations techniques to solve major chemical processing challenges. These include phase transfer technologies (ion exchange, solvent extraction), membrane technologies (electrodialysis, reverse osmosis), supercritical fluids, and electrochemical technologies (electrochemical ion exchange, electrokinetics, electrochemical deposition, and electrochemical conversions). The Laboratory directs basic science capabilities to address fundamental research issues in the areas of supercritical fluids, electrophoresis, capillary electrophoresis, colloidal chemistry, and materials science and characterization. Integrated project teams that consist of scientists, industrial chemists, and process engineers collaborate to develop and deploy separation technologies to solve complex environmental problems. The Laboratory's expertise includes testing of materials and adaptation of technologies to improve processing.

Ion Exchange

The Laboratory has led major research and development advancements in the areas of ion exchange and solvent extraction through nonradioactive and radioactive testing. Ongoing research ranges from small-scale laboratory development to pilot-scale demonstration to full-scale design and deployment of a variety of systems. Directed research activities are being conducted to study the structure/function relationships of separating agents, develop and synthesize new agents, and determine chemical stability.

Innovation in both application and deployment has been key to the Laboratory's capabilities and contribution in the area of ion exchange. The Laboratory's engineering activities include evaluating complete systems and designing full-scale operations. The Laboratory recently designed the ion exchange system for DOE's West Valley Demonstration Project, which included developing a new exchanger and designing a system for in-tank deployment. The Laboratory also invented the Waste Acid Detoxification and Reclamation System, which uses a conventional distillation process with newly developed materials to recover and reuse waste acid.

Electrochemical Processing

The Laboratory's electrochemical processing work has involved both separation and conversion processes. Separation processing has focused on the partitioning of charged ionic species using electrodialysis, electrochemical ion exchange, electrokinetics, and traditional electrochemical deposition. The diversity of the Laboratory's techniques allows selective ionic separation for gas, liquid, and solid phases. These techniques have been applied to hazardous and mixed waste, industrial waste streams, soil remediation, and fundamental ionic transport characterization. The Laboratory has performed demonstrations at both laboratory- and bench-scales. The Laboratory also has developed both direct and indirect electrochemical oxidation/reduction processes for the electrochemical separation/conversion of hazardous and mixed wastes.

In addition, the Laboratory has developed non-thermal treatment alternatives for the conversion of organic compounds and decomplexation of radionuclides in Hanford tank waste and developed processes such as Catalyzed Electrochemical Plutonium Oxide Dissolution (CEPOD) to separate and concentrate plutonium oxide from waste streams. Both simulant and radioactive waste streams are used to evaluate electrochemical treatment processes. Ongoing research ranges from small-scale laboratory development to pilot-scale demonstration and full-scale design. The Laboratory also offers a broad range of electroanalytical capabilities to support the development of these process technologies.

Membranes

The Laboratory is conducting research and development on all aspects of membrane development, from synthesis of new and novel membranes for highly selective separations to engineering evaluation of membrane degradation and fouling. We have also developed and tested the selective separation of metals, organics, and gases using membranes.

Instruments, Equipment, and Facilities

A key strength of the Laboratory's capabilities is its proximity to Hanford, which allows access to actual waste for process testing. The Laboratory has facilities available for work with hazardous and radioactive materials including simulants and actual wastes.

For ion exchange we have a laboratory-scale ion exchange system (6 columns). These 200-mL columns are capable of testing ion exchange materials in realistic process configurations using waste simulants with radioactive tracers. These have been used successfully in the design and operation of the WVNS supernatant system. Additional ion exchange columns for evaluating industrial separations are available in our onsite Applied Chemistry Laboratory.

The Laboratory's electrochemical separations equipment ranges from fundamental rotating-disk electrodes to bench-scale processing facilities. Both the laboratory and bench-scale equipment include batch and continuous operation. Specific equipment includes

- potentiostat/galvanostats for traditional electrochemical voltammetry experiments, which accommodate low-level current measurements (nanoamps) and high-level current delivery (10 amps)
- mass transfer controlled electrodes, including rotating disk electrodes and rotating ring-disk electrodes
- bipotentiostat/galvanostat for rotating-disk electrodes
- wave and pulse generators
- continuous electrodialysis cells, including micro flow cells (four compartments) and bench- scale flow cells (nine compartments)
- Electrochemical ion exchange cell (three compartments)
- laboratory and bench-scale electrochemical cells with supporting equipment (projected electrode areas 0.001 m^2 to 0.2 m^2)
- pilot-scale mediated electrochemical oxidation unit in a High Bay facility (1.8 m^2 projected electrode area) (see Figure 4).
- pilot-scale CEPOD unit located in a glove box
- controlled Potential Coulometry units
- electrochemical quartz crystal microbalance for electrode interfacial characterization (vector impedance meter)
- numerous ion exchange membranes, electrode geometries, and custom electrochemical cells.

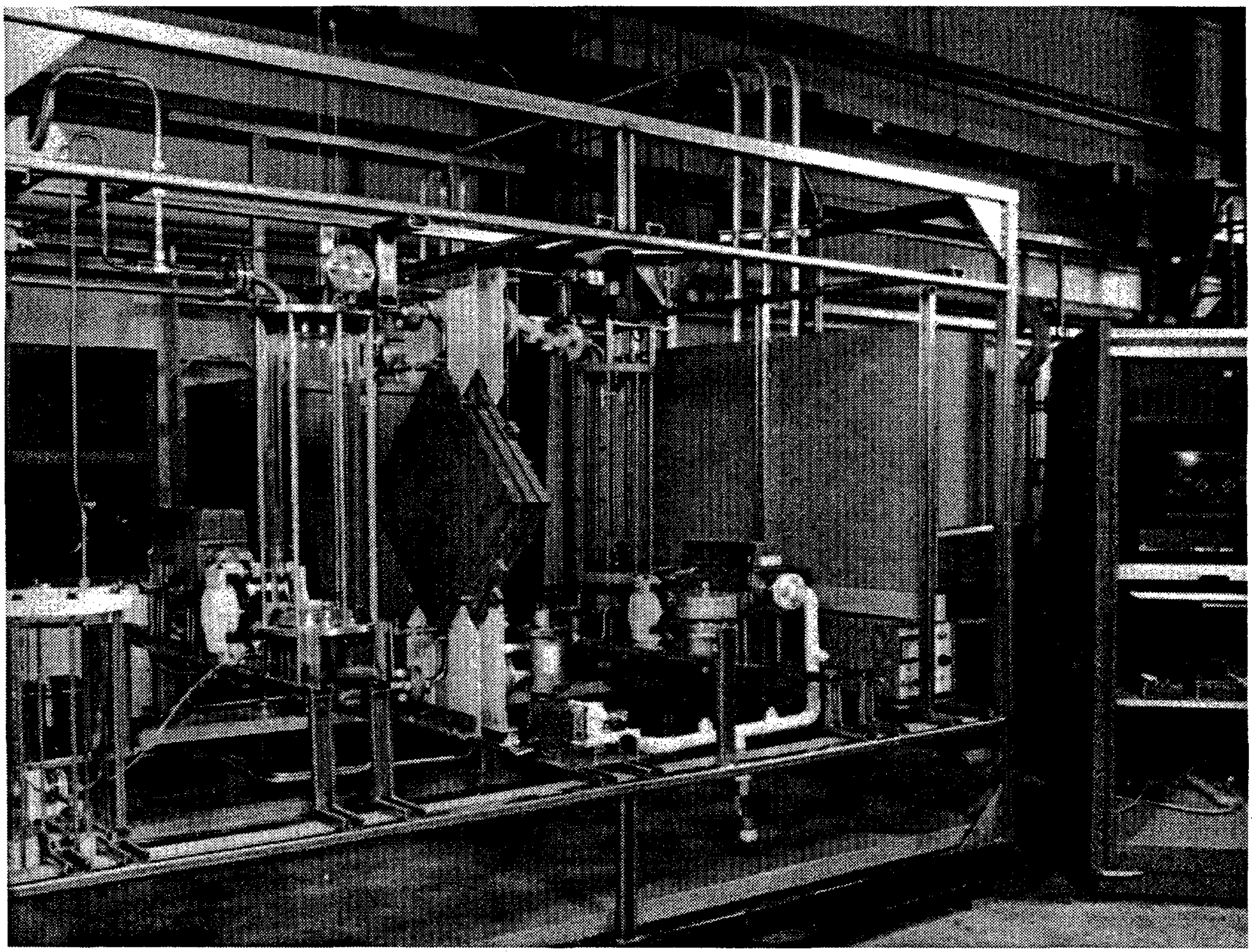


Figure 4. Pilot-Scale Mediated Electrochemical Oxidation Unit in a High Bay Facility.

Thermal Processing

The Laboratory has been a recognized leader of waste vitrification technology since the late 1960s, when development focused on high-level radioactive wastes. Since that time, the Laboratory has developed several waste vitrification technologies including calciner-melter combinations (spray, fluid bed, and wiped film evaporator); simple melters such as in-can melters, both metallic and ceramic-lined, for the vitrification of radioactive wastes; and the LFCM. The LFCM technology has been adopted worldwide as the reference technology for high-level waste vitrification. The Laboratory has successfully developed and transferred vitrification technology "know-how" to the Savannah River Site, West Valley Demonstration Project, Japan, and Germany.

Waste Form Development and Performance Testing

The Laboratory has developed glass science in conjunction with the melter technologies and has established fully staffed waste form development, modeling, and testing laboratories. State of the art facilities are available in the areas of 1) glass and melt characterization; 2) surface and microscopic analysis; 3) leaching and durability; 4) chemistry, redox, and structure; and 5) mechanical properties and characterization. The facilities and equipment currently available are highlighted below (*denotes both radioactive and cold sample capabilities currently available). Quality assurance and good working practices are applicable to all work conducted in these facilities. In addition, statistically and theoretically based models have been developed which greatly aid and optimize waste form development and repository performance efforts.

Glass and Melt Characterization:

- Glass melting from waste feeds or other raw materials:*
  - high temperature furnaces (to 1700°C)*
  - controlled atmospheres*
  - direct observation of melting (quartz crucible furnace)

- Laboratory studies of batch conversion:
  - off gas analysis (GC/MS)*
  - observation of ablation (ablation furnace)
  - characterization of batch to melt interface (microscopy)
  - quench in techniques for isothermal and non-isothermal kinetics*
  - thermal analysis (DTA/TGA)
  - scale up capabilities*

- Volatility:
  - thermal off gas analyzer
  - DTA/TGA/MS with Knudsen cell and heated transfer line
  - thermodynamic calculation of vapor pressures (FACT)*

- Complete viscosity characterization:
  - spindle viscometers (10^{-3} to 10^{3} Pa.s up to 1700°C)*
  - beam bending viscometer (10^{7} to 10^{13} Pa.s up to 1000°C)
  - extensive data base of viscosity/ temperature/composition*
  - viscosity prediction and modeling*

- Electrical conductivity:
  - in melt electrical conductivity probe*
  - impedance spectroscopy (1 to 10^{6} Hz up to 1700°C)*
  - automated data analysis*
  - database and modeling/prediction capabilities*

- Liquidus temperature:
  - gradient furnaces (to 1550°C)
  - low linear gradient ($\leq$1°C/mm)
  - uniform temperature furnaces (to 1700°C)*
  - thermodynamic calculation of liquidus temperature developed and proven for complex nuclear waste glasses (FACT)*

- Crystallization kinetics:
  - isothermal and non-isothermal kinetic techniques*
  - gradient furnaces (to 1550°C)
  - differential thermal analysis (to 1500°C)
  - prediction of crystal concentration as a function of location within waste canister or other waste form geometry subjected to complex cooling schedules

Surface and Microscopic Analysis:

- optical microscopy (OM):*
  - digital image analysis*
  - 4 to 1000X calibrated three dimensional measurements

- scanning electron microscopy (SEM):*
  - environmental (high pressure) analysis
  - image analysis and video recording
  - high temperature stage (to 1000°C)
  - wave length dispersive spectroscopy (WDS)
  - quantitative energy dispersive spectroscopy (EDS)*

- transmission electron microscopy (TEM):*
  - 300 KeV field emission source
  - high energy EDS*
  - electron energy loss spectroscopy (EELS)

- Surface spectroscopy:
  - secondary ion mass spectroscopy (SIMS)
  - Auger spectroscopy
  - electron spectroscopy for chemical analysis (ESCA)

- Other surface techniques:
  - atomic force microscopy (AFM)
  - langmuir analysis (BET)
  - zeta potential and mobility in dilute or concentrated slurries
  - particle size distribution (microtrack light scattering and wet/dry sieving)*

Leach and Durability:

- Tests:
  - product consistency test (PCT)*
  - materials characterization center test (MCC-1)*
  - standard flow-through dissolution (saturated matrix)*
  - unsaturated flow-through dissolution (open porosity)*
  - forward rate of dissolution as f(pH, solution chemistry, and temperature)*
  - vapor phase hydration testing*
  - TCLP*

- Extensive database and modeling/prediction capabilities:*

- Performance assessment:*
  - geo-chemical codes*
  - thermodynamic database*

Chemistry, Redox, and Structure:

- Chemical analysis of glass and feed:
  - fusion*
  - inductively coupled plasma spectroscopy (ICP/AE, ICP/MS)*
  - atomic absorption spectroscopy (AA)*
  - x-ray fluorescence (XRF)*
  - ion chromatography (IC)*
  - x-ray photoelectron spectroscopy (XPS)
  - selective ion electrodes (SIE)
- Bonding, chemistry, and structural spectroscopy:
  - Raman
  - Fourier transform infra-red (FTIR)
  - nuclear magnetic resonance (NMR)
  - ultra violet/visible light (UV/VIS)
  - x-ray diffraction (XRD)*
- Redox:
  - Mössbauer
  - wet chemistry*
  - UV/VIS

Mechanical Properties and Characterization:

- Density:
  - thermal expansion measurement, thermal mechanical analyzer (TMA)
  - geometric*
  - Archimedes*
  - databases and models for prediction of density and thermal expansion*
- Microhardness indentation (Vickers and Knoop)
- Fracture strength
- Moduli:
  - constant strain analysis (Instron)
  - constant load analysis
  - strain gauge
  - models for prediction of moduli

Process Engineering and Demonstration

Technology development experiences have included adapting vitrification technology to meet the many needs for other types of wastes including low-level wastes, municipal solid waste, medical waste, hazardous wastes, sludges, and soils. The Laboratory has designed 23 integrated vitrification systems including the radioactive LFCM that vitrified 22 MCi of radioactive material for the German government, three high-temperature melter systems capable of vitrifying materials at 1500°C. Currently, more than 45 staff are involved in low-level and high-level waste thermal processing technology such as design, flowsheet and process development, remote operations, and numerical and computational modeling. Many of these staff provide a technical and historical continuity extending back to the initial developments of LFCMs and borosilicate glass.

The Laboratory's vitrification facilities include the Engineering Development Laboratory (EDL) in the 324 Building where a laboratory with 2,200 sq. ft. of floor space has been converted to vitrification development in support of radioactive wastes using nonradioactive simulants. This facility houses a Pilot-Scale High-Temperature Melter, Small-Scale High Temperature Melter, and Research-Scale Melter (see Figure 5). Laboratory staff were responsible for the engineering, design, construction, operation, and evaluation of the vitrification processes currently in operation.

Significant attention must also be given to feed stream preparation/feeding and off-gas treatment equipment needs. Fully representative full-scale and tenth-scale DWPF/HWVP feed preparation tanks, condensers, sampling station, and pumping equipment are housed in the 324 building High Bay. Current off-gas capabilities supporting the EDL and the High Bay include

- 800 SCFM capacity blower
- Submerged-bed and ejector venturi primary scrubbers
- High-efficiency mist eliminator
- Hydrosonic scrubber
- Thermal syphon evaporator
- Packed column
- High-efficiency metal fiber filter
- High-efficiency particulate air (HEPA) filter
- Activated carbon absorption.

Characterization of the process during operation includes state-of-the-art computer data acquisition equipment to log and manipulate direct-measured parameters such as temperatures, pressures, flows, etc. Physical and chemical analyses of simulants, and refractory and electrode materials

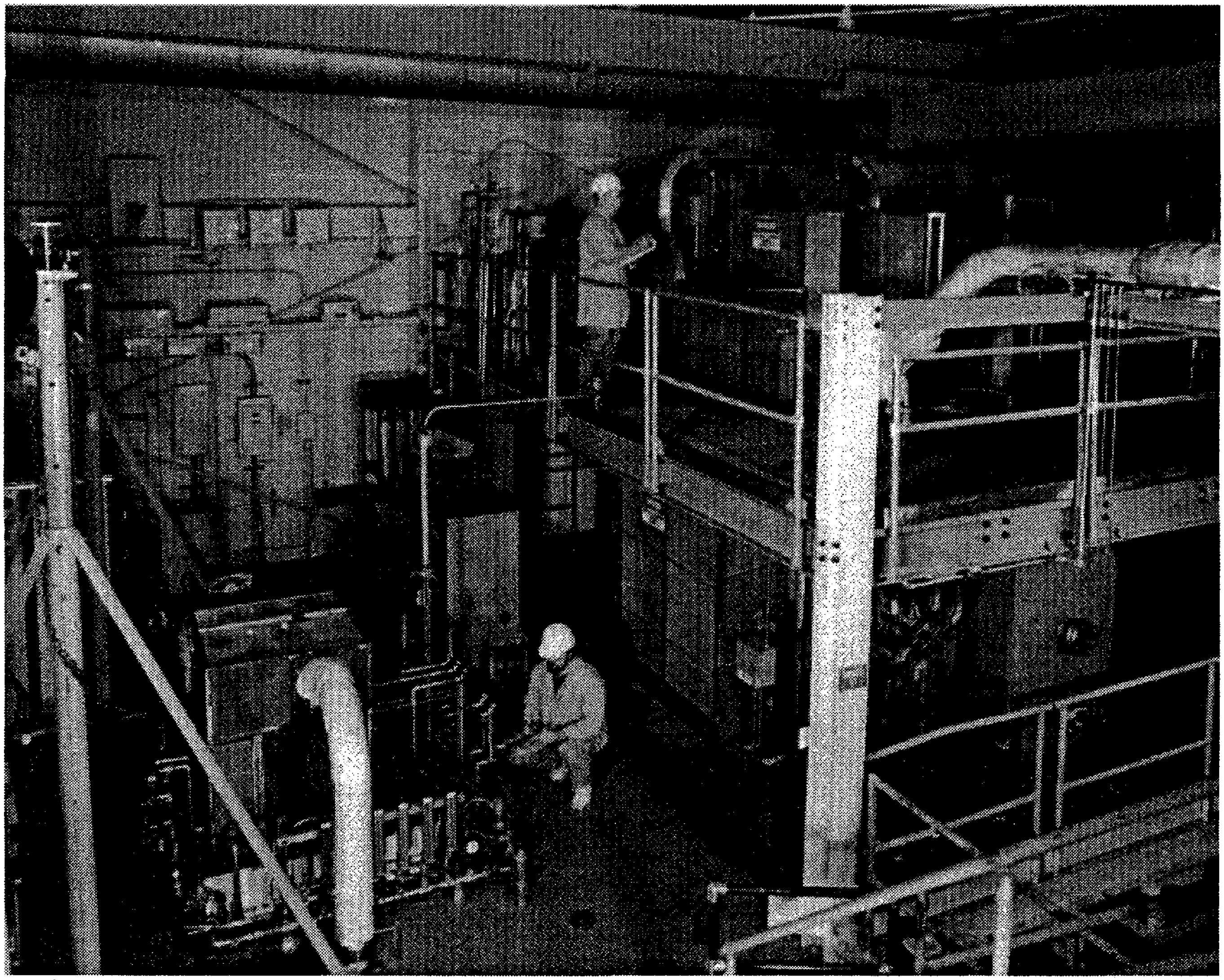


Figure 5. Small-Scale High-Temperature Melter (left) and Pilot-Scale High-Temperature Melter (right).

evaluations (electrochemical as well as coupon studies), support the process testing efforts. Measurement of aerosol, gaseous, and particulate are a key function of the engineering laboratory. Representative equipment include

- On-line continuous gas monitors for noncondensible gases such as CO, H_2, NO_x, N_2O
- GC/MS
- Isokinetic particulate samplers
- On-line aerosol analyzers
- Condensible gas scrubber samplers.

Radiochemical Processing

For over a decade the Laboratory has provided waste separations and immobilization support to Hanford operating contractors. Much of the development and testing has been performed with samples of actual Hanford waste. Recent waste separations process testing has concentrated on washing, filtration, and decantation with emphasis on ion exchange. The separated species are formulated and then converted to vitreous and other specific waste forms prior to characterization. The Laboratory's expertise in radiochemical processing includes remote, radioactive pilot scale development and testing of chemical and radiochemical systems. The Laboratory also develops process flowsheet design, and installs and tests radiochemical process systems that include leaching, solvent extraction, ion exchange, vitrification, fuel dissolution, decontamination, evaporation, grouting, solid waste packaging and shipment, and high-level liquid waste shipping, receiving, and transportation.

Instruments, Equipment, and Facilities

The Laboratory's state-of-the-art radiochemical processing instruments (see Figure 6) and facilities include

- large shielded chemical process development hot cells with stainless steel liners, including one multi-story cell
- a remote in-cell electropolishing unit that can decontaminate (to below background) items as large as 30 inches in diameter by 10 feet in length
- full-scale and pilot-scale slurry testing equipment and 1/10 scale vitrification pilot plant system (non radiative)
- pilot-scale hydropulse filtration pilot plan to simulate radioactive testing
- remote in-cell grouting, welding, encapsulation, and helium leak testing capability
- remote fuel and target disassembly/sectioning and packaging
- remote in-cell glass leach testing and radioactive glass sample preparation
- two low-level, hands-on radioactive bench-scale test facilities
- large-scale sludge retrieval pilot plants at 1/12 and 1/4 scale of Hanford waste tanks
- a sludge simulant development laboratory.

Points of Contact

For questions regarding Laboratory technical capabilities, interested parties are encouraged to contact:

William F. (Bill) Bonner, Program Manager
Separations and Waste Forms
Box 999, MS K9-14
Richland, WA 99352
509-372-6263 (work)
509-375-5963 (fax)
E-mail: wf_bonner@pnl.gov

Walter C. (Wally) Weimer, Program Manager
Analytical Chemistry and Spent Fuel Behavior Group
P.O. Box 999, MS P7-27
Richland, WA 99352
509-376-3995 (work)
509-376-2870 (fax)
E-mail: wc_weimer@pnl.gov

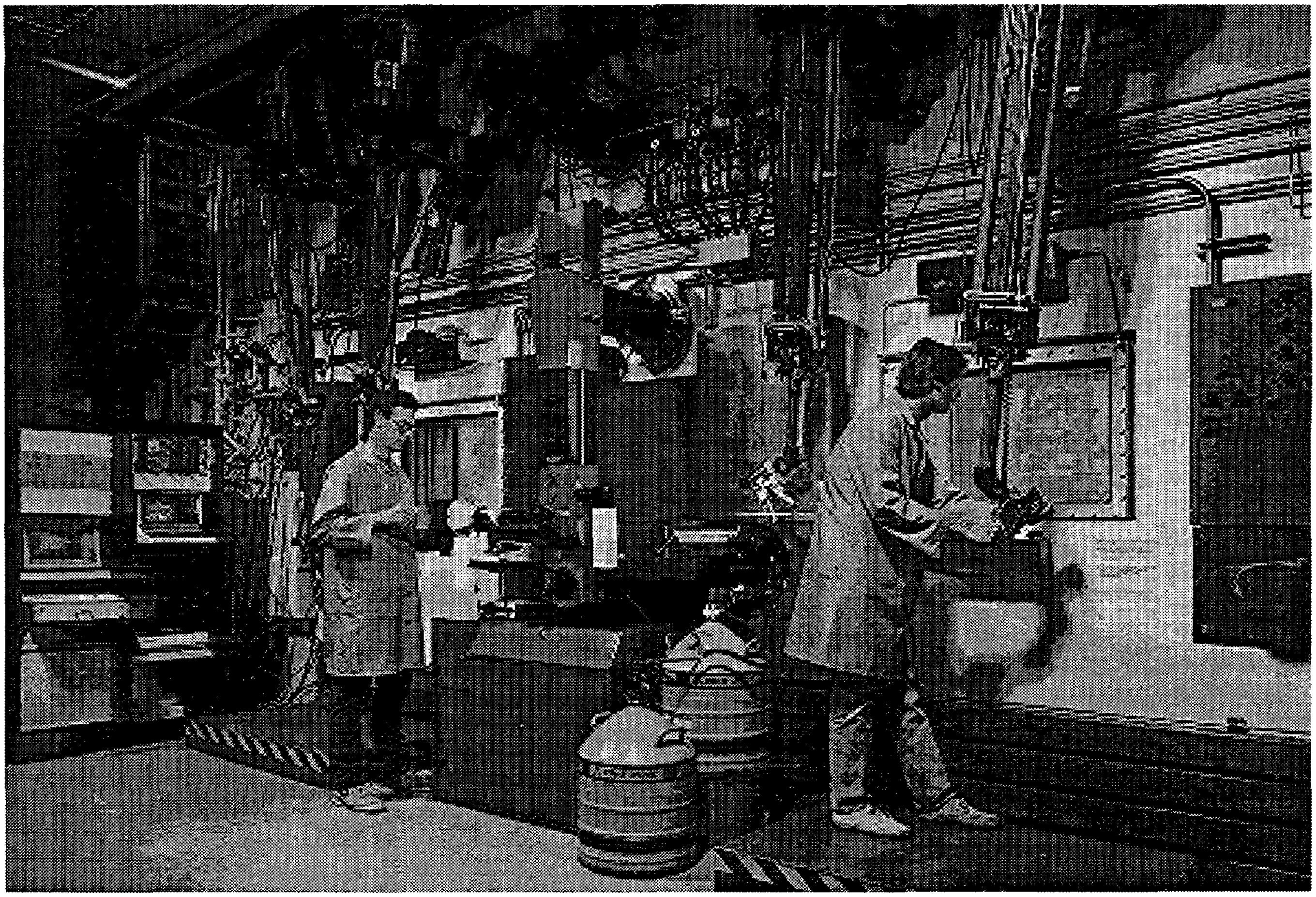


Figure 6. Radiochemical Processing Cells.

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
by Battelle