EMSP

Environmental Management Science Program

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CHARACTERIZATION AND SAFE STORAGE OF HIGH-LEVEL WASTE

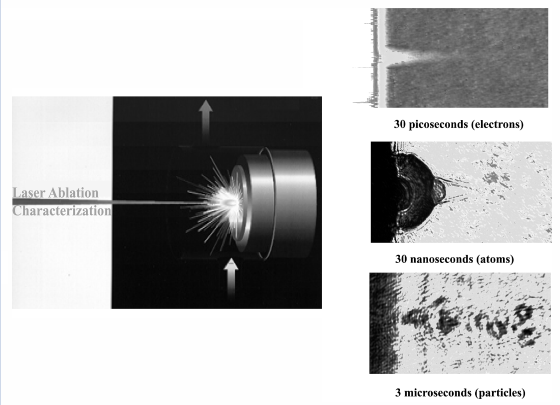
Characterization of tank wastes is important for all tank remediation efforts. Safety issues prior to remediation must also be understood.

The characterization of the materials in high-level waste tanks is important for all remediation procedures. Projects related to tank waste characterization include:

- An investigation of the chemistry of lanthanide ions in highly basic solutions as well as an exploration of new agents for extracting metal ions from solids and gels.
- A study of the chemistry of strontium and actinides under the extreme conditions found in the tanks.
- The development of a new type of sensor with one potential application being the detection of ferrocyanides in tanks.
- Potential applications of seismic measurements to define properties such as the layering, fraction of solid and liquid phase, and presence of interstitial gas in the material inside tanks.
- Fundamental studies of laser-ablation processes to improve the accuracy of a widely used analytical technique.

All of the projects related to tank safety have explored issues related to the formation or venting of gases in tanks:

- Studies of mechanisms of radiolysis in tanks have shown how sodium nitrate is involved in the formation of gases and how materials such as grout may contribute to radiolytic aging.
- A detailed modeling and experimental study was designed to explore the consequences of an extended failure of the ventilation system in a tank.
- The nitrogen-oxygen chemistry that results from the radiolysis of concentrated solutions of nitrates and nitrites has been explored in one project, and the role of aluminum compounds as catalysts for the oxidations of organic species in the tanks has been explored by another.



Characterization of Materials in High-Level Waste Tanks
An LBNL project (55318) has studied laser-ablation processes to ensure accuracy of characterization using non matrix-matched standards. The images at right show ejection of electrons, atoms, and particles at different times during an ablation event. Understanding the contribution of each mass form to the chemical analysis is a research goal.

Problems/Solutions

- As stated in a Tanks Focus Area Science Needs statement, "the development of calibration standards, calibration procedures, and method validation for laser ablation inductively coupled plasma mass spectrometry for radioisotope analysis in wastes is required." These are the goals of an EMSP project.
- The production of hydrogen and other gases in high-level waste tanks is a primary safety concern. An EMSP project is investigating some fundamental aspects of radiolysis in materials similar to those in the tanks to aid in the continued development of safe processing strategies. Another project is investigating the mechanisms of some nonradiolytic, chemical mechanisms for the production of gases in tanks.
- Electrochemical sensors tend to be sensitive, but not selective enough for use in complex mixtures. A new hybrid sensor uses an optically transparent electrode that is coated with a selectively permeable film, so selectivity is obtained by the optical measurement, the selective transport of materials to the electrode, and the selectivity provided by electrochemistry.

Anticipated Impact

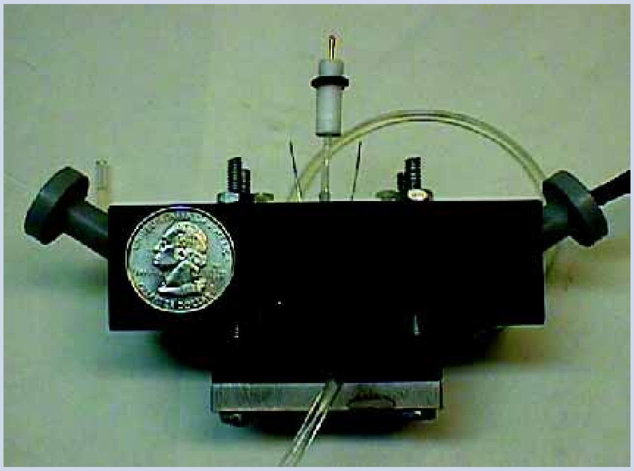
- An 80,000-gallon tank of high-level waste at Mayak, Soviet Union, exploded in 1957, resulting in the contamination of 9,000 square miles in the vicinity, 75 square miles of which remain uninhabitable today. Thus, a thorough understanding of the generation and venting of hydrogen is particularly important for safe operation of the 177 tanks at Hanford (average capacity over 700,000 gallons each) and the 49 tanks at Savannah River (average capacity over 1,100,000 gallons each).
- A large amount of low activity waste has been or is planned to be stored in grout. An EMSP study has shown that grout and saltstone may actually lead to more efficient radiolysis of residual water, along with its adverse effects.

Characterization of Materials in High-Level Waste Tanks

High-level waste in tanks has been made highly basic in order to minimize tank corrosion, but under these conditions the waste exists in a complex mixture of solids, gels, and solutions. The goal of the University of New Mexico project (54595) is to understand the coordination chemistry of the relevant metal ions in highly basic solutions. They have studied hydrolysis reactions of some lanthanide ions in basic solutions in the presence of several common anions, and they have investigated some new complexing agents that show promise for extracting metal ions from the solids and gels present at high pH values. Such agents could lead to a considerable reduction in the volume of material that needs to be treated as high-level waste.

The PNNL/Florida Sate project (54621) has investigated the chemistry of strontium and actinides under conditions similar to those found in the high-level waste tanks. Their studies of strontium speciation indicated that metal ion displacement reactions are an alternative to costly and hazardous organic destruction technologies for reducing the impact of organic chelating agents in tank processing. Their studies of an actinide surrogate, europium, in highly basic solutions in the presence of organic complexing agents showed why older models underpredicted solubilities by two to four orders of magnitude. Studies of solution phase calorimetry, activity coefficients at high electrolyte concentrations, and electrophoresis-mass spectrometry studies have also led to improved fundamental understanding of the chemistry of metal ions under the extreme conditions found in the tanks.

About 140 metric tons of ferrocyanide were added to some Hanford tanks more than 40 years ago to remove cesium from tank waste liquids. Although much of the ferrocyanide may have decomposed, a reliable sensor that can function in the tanks will be useful for characterization prior to retrieval operations. The University of Cincinnati group (54674) has developed a new hybrid sensor consisting of an optically transparent electrode that is coated with a film that selectively allows transport into the detection region. Selectivity is obtained by choosing the coating material, the electrolysis potential, and the wavelength of light that is used as the detector for the electrolysis product. The sensor concept has been applied to the detection of several analytes, including ferrocyanide in a waste-tank-simulant solution, and a sensor package has been developed for use with a Hanford tank sample.



Characterization of Materials in High-Level Waste Tanks
Technology developed by a University of Cincinnati project (54674) has led to a portable spectroelectrochemical sensor, shown above. Using three modes of selectivity, detection is accomplished with a sample volume of 800 microliter.

The MIT project (55141) is exploring potential applications of seismic measurements for tank characterization. Prior to beginning this project, some measurements had been made in a tank that had two liquid observation wells. Because most tanks have only one well, this project was designed to explore seismic measurements in which a source is placed on the surface outside a tank and a hydrophone string is placed in the single liquid observation well. Modeling studies for a tank with a single fluid layer were found to be in fairly good agreement with scaled measurements on small tanks. The normal modes were found to be especially useful when the vertical array of hydrophones is not on the center line of the tank, which is the case with many Hanford tanks. It was also shown that measurements in a tank should be made at high frequencies to obtain information on properties such as the layering, fraction of solid and liquid phase, and presence of interstitial gas in the material inside the tanks. The basic studies completed so far were necessary before attempting these more complex tasks.

One of the characterization goals for the Tanks Focus Area is to “optimize and upgrade laser ablation/mass spectrometry equipment and procedures for quantitative elemental analysis of solid samples.” The EMSP project at LBNL (55318) is directed toward fundamental studies of laser-ablation processes in order to improve the reliability of analytical techniques that use this method to characterize a sample. Studies of the effects of particle size distributions, fractionation, and matrix composition on the reliability of inductively-coupled-plasma mass spectrometry signals have been performed. Ongoing work is directed toward achieving accurate analysis without the use of matrix-matched standards, which would greatly reduce the complexity and cost of tank waste analyses.

Safe Storage of Tank Wastes – Formation of Gases in Tanks

The generation of hydrogen and other gases in high-level waste storage tanks is one of the primary concerns related to tank safety. Some fundamental aspects of the mechanisms of radiolysis in tank wastes are the subjects for the PNNL/University of Notre Dame project (54646). They have shown that the radiolysis products from sodium nitrate crystals are similar with electron-stimulated and photon-stimulated desorption, and this has enabled them to simulate radiolytic processes more easily. They have investigated the primary radiolytic products in these crystals and shown how these products can lead to the production of nitrous oxide and other compounds that lead to the formation of hydrogen gas in the tanks. They have also shown how radiolysis of liquids that contain colloidal oxide particles can lead to the production of hydrogen in the vicinity of the particles. Thus, they conclude that heavily solids-laden wastes may contribute to, rather than deter, radiolytic aging, that long-term storage in grout or saltstone may lead to more efficient radiolysis of water, and that preferential generation of gaseous products may occur in tanks following draining operations.

Radiolytic hydrogen and other flammable gases are removed from high-level waste tanks by purging and ventilation systems, but what would be the consequences of an extended failure of those systems? The University of California – Berkeley project (54656) has involved both experimental and modeling studies of the mixing processes that can affect the distribution of fuel and oxygen in high-level waste tanks. The experimental work was conducted using small tanks with simulated tank solids and helium as a hydrogen simulant, and the primary objective was to simulate how a plume of air would enter a tank from openings in the ceiling and how much air would reach the liquid surface. Previous models developed for enclosure fires were not considered adequate for assessing the potential for accumulation of high-concentration pockets of oxygen and flammable gases in the tanks, and more general computational models were being developed and compared to the results from the experimental simulations.

A University of Notre Dame/PNNL project (55229) has concentrated on the nitrogen-oxygen chemistry that results from radiolysis of concentrated aqueous solutions of nitrates and nitrites. Most of the primary radicals produced by the irradiation of highly concentrated waste simulant solutions are rapidly converted to NO_2 or NO. Their primary focus has been on the fate of reducing radicals and the products NO_2 and NO. The major reducing radical is the nitrate dianion. It is metastable and converts through reaction with water and other proton donors to nitrogen dioxide, NO_2, without generation of hydrogen under conditions of the tank wastes. The NO_2 radical is oxidizing in character. Their work shows that it is the dominant species responsible for oxidation of organic compounds in the tanks.

The Georgia Tech project (54807) is also focused on the chemical processes that can lead to the production of gases in tanks. Tanks that evolve gases all contain nitrates, nitrites, and aluminum hydroxide under highly basic conditions along with organic complexing agents. Earlier work suggested that the anion NO^- should be an intermediate in the reaction of nitrites with the metal complexing agents, and a major goal of this project has been to study reactions of NO^-. Synthesis of several possible precursors to NO^- have been explored, but a satisfactory route to rapid production of NO^- had not yet been found. The role of aluminum compounds as catalysts for the nitrite oxidations of organic species to produce gases has also been investigated. An analysis of the relative contributions of thermal versus radiolytic pathways for some organic compounds in the tanks suggested that as much as 95% of the decomposition of one compound (glycolate) occurred by thermal pathways, whereas only 15% of another (HEDTA) was by that route.

Project Teams

Lead Principal Investigator (Award Number)

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- Massachusetts Institute of Technology
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