EMSP
Environmental Management Science Program
Project Summary Fact Sheet • April 2000

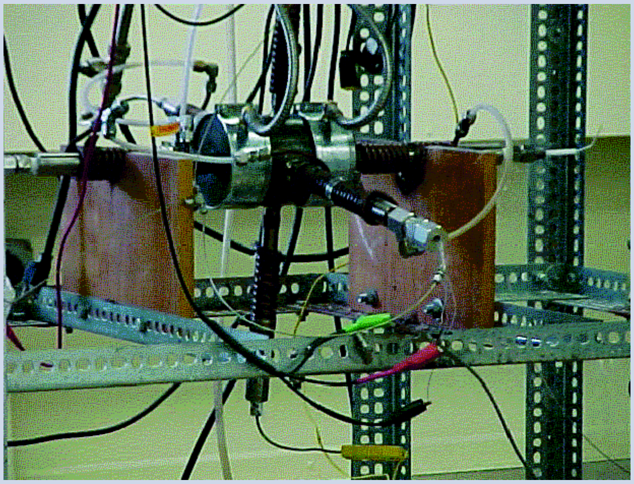
ANALYTICAL CHEMISTRY AND INSTRUMENTATION

IMPROVEMENTS IN CHARACTERIZATION TECHNIQUES MEET HIGH-PRIORITY NEEDS IN ALL DOE ENVIRONMENTAL MANAGEMENT PROGRAMS

Characterization methods are high priorities for most remediation programs. For example, the Mixed Waste Focus Area's highest priority is to improve the reliability of nondestructive examination and assay techniques. The Tanks Focus Area has cited thorough characterizations of tank wastes as a prerequisite to all treatment processes, and the Deactivation and Decommissioning Focus Area has characterization needs in each of its four major product lines.

Many EMSP projects are oriented toward fundamental problems of importance in each of these areas:

- A thousand-fold increase in the sensitivity of neutron-based characterization methods could result if an EMSP project to develop an improved neutron source is successful.
- The objective of one EMSP project is to better understand the fundamentals of the laser ablation technique to provide rapid, cost-effective, and accurate characterization of EM waste site samples.
- There have been numerous studies of the complexation chemistry of positively charged ions (cations), but an EMSP project is exploring the design and synthesis of anion-complexing species. Another project has focused on inorganic materials to separate strontium and cesium from other tank wastes.
- The improvement of selectivity of sensors is a major area of interest in analytical chemistry, and potential applications of molecular recognition techniques are at the forefront of research in this area. Some of the leading researchers in this area are involved in an EMSP project that is developing sensors for heavy metal ions. Sensors that are applicable in hostile environments are also of interest, and another project is attempting to develop reliable monitors for use in the particularly corrosive environment of supercritical water.



Development of Monitors for Supercritical Water Environments
Supercritical water has been explored as an oxidizing agent for hazardous organic compounds by a Pennsylvania State University project (55171). This photo shows a titanium thermocell for pH and electrochemical noise measurements in high-temperature subcritical and supercritical aqueous solutions.

PROBLEMS/SOLUTIONS

- A thousand-fold improvement in the flux from a small neutron source could greatly improve nondestructive characterization limits for the thousands of drums in the U.S. Department of Energy (DOE) inventory.
- The development of selective complexing agents for anions may lead to the first significant applications of dual receptors for the selective removal of salts from mixtures.
- Even though organic complexing agents may be effective in selective removal of species from solutions, the resulting species may be difficult to convert to a form suitable for permanent storage. If effective inorganic complexing agents can be found, then less post-separation treatment would be necessary.
- Sensors for metal ions that use changes in luminescence properties are frequently very sensitive, but they tend to have limited applicability because they respond to many different species. The incorporation of molecular recognition units into a polymer may provide a means to make a variety of sensors for individual organic and metal species.

ANTICIPATED IMPACT

- About 140 metric tons of ferrocyanides were added to waste now contained in 18 Hanford tanks, but some of it may have decomposed during the past 40 years. Nevertheless, a reliable sensor for ferrocyanide that can function in a waste tank will be helpful during retrieval and immobilization of tank wastes.
- To avoid unnecessary storage of waste materials in high-level repositories, it is necessary to have accurate nondestructive assays of low-level wastes. A new high fluence neutron source being developed by an EMSP project could provide the means to perform such assays.
- New agents that could remove surface contaminants could enable economical recovery and reuse of metals worth millions of dollars.

Technical Summary and Progress

Development of a New Hybrid Spectroelectrochemical Sensor

The University of Cincinnati group (54674) has developed a new hybrid sensor. To be detected, an analyte must pass through a selective coating and then be electrolyzed at the potential applied to an electrode. Either the analyte or its electrolysis product must absorb light at the chosen wavelength. Thus, selectivity is obtained by choosing the coating material, the electrolysis potential, and the wavelength. The sensor concept has been applied to the detection of several analytes, and a sensor package has been developed for use with a Hanford tank sample.

High Fluence Neutron Source for Nondestructive Characterization of Nuclear Waste

The objective of the LANL project (54751) is to develop a source at the 10^{11} neutron/second level to enable a thousand-fold increase in the sensitivity of neutron-based characterization methods. The target is a device that costs about \$100 K and that can operate for 10,000 hours with a 10-kilowatt power consumption. A triple grid design is intended to enable production of a plasma at lower densities so that a collisionless plasma with high energy, beam-beam collisions can be achieved. Accelerating voltages of about 75 kilovolts (kV) are required to reach the fusion threshold for D-D and D-T fusion reactions, and 52 kV was achieved by June 1999.

Chemistry of Selective Anion Recognition

Most selective agents for separations or sensors form complexes with cations, but the University of Kansas/ORNL project (54864) is directed toward the design and synthesis of species to form complexes with anions, such as nitrate or pertechnetate. Several large cyclic molecules have been found to bind nitrate ions, for example, and coworkers at ORNL have used a combination of cation and anion complexing agents to extract cesium nitrate.

Inorganic Processes to Treat Radionuclides

The University of Washington project (55146) has focused on inorganic materials for removal of strontium and cesium from other constituents in Hanford tank wastes. Iron-oxide-coated sand was used in columns to remove strontium from simulated wastes, and it was found that the columns could be regenerated and reused. An electrochemically controlled system was being explored as a method for removing cesium. Preliminary experiments showed promise for cesium removal although it may not be possible to use the system at the very high pH values typically found in the tanks.

Development of Monitors for Supercritical Water Environments

Above the critical temperature and pressure for a substance, liquid and gaseous phases are not distinguishable, and supercritical fluids are being investigated for several applications. Supercritical water has been explored as an oxidizing agent for hazardous organic compounds. The Pennsylvania State University/INEEL project (55171) has been directed toward development of a flow-through electrochemical cell that can be used to make reliable pH measurements and to monitor corrosion processes on metals exposed to supercritical water.

Sensors Using Molecular Recognition in Polymers

The aim of the ANL/University of California – Berkeley/Tufts University project (55247) is to develop sensors for detecting specific heavy metal ions. The strategy is to incorporate selective metal ion binding agents into a polymer such that changes in the optical and/or conductive properties of the polymer occur when a metal ion is bound. A number of different polymers have been prepared, and ligands that are specific for iron, plutonium(IV), uranyl, and lead ions have been made. High selectivity for Pu(IV) complexation was demonstrated with one of the resins prepared. Other work using similar polymers has been directed toward preparation of fiber optic sensors for metal ions.

Fundamental Development of Laser Ablation Technology

The laser ablation technique is ideally suited for sampling small quantities of solids for subsequent analysis by mass spectrometry techniques; the technology is being used at most major DOE laboratories. The accuracy and precision of the ablation process is dependent on the nature of the materials in the sample. Calibrations with standards very similar to the unknown samples have been required for accurate determinations. Unfortunately, it is often very difficult to prepare such reference standards for samples of interest in the DOE complex. The LBNL project (55318) is directed toward exploring the fundamentals of laser ablation to improve the quantitative accuracy of the technique and establish calibration by using non matrix-matched standards.

Project Teams

Lead Principal Investigator (Award Number)

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