WP-11

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

PRETREATMENT OF HIGH-LEVEL WASTE

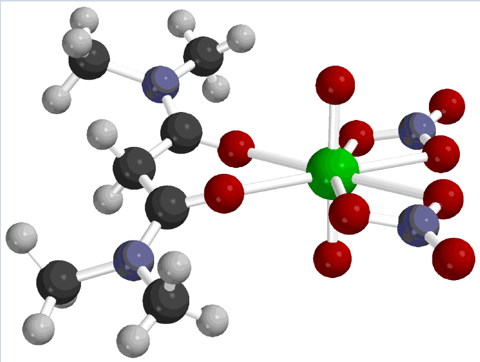
EFFICIENT REMOVAL OF RADIONUCLIDES AND OTHER SPECIES IN TANK WASTES IS NECESSARY TO MINIMIZE THE VOLUME OF MATERIALS THAT REQUIRES LONG-TERM STORAGE

The total volume of waste in large, underground storage tanks at U.S. Department of Energy (DOE) sites is approximately a hundred million gallons. Even in tanks with very high levels of ionizing radiation, radionuclides are only a very small fraction of the total mass in the tanks. Thus, pretreatment processes that separate radionuclides (particularly cesium-137, strontium-90, technetium, and some lanthanides and actinides) from the bulk of the tank material are essential for economically viable immobilization of the high-level waste. Some EMSP projects in this area include:

- design and synthesis of diamides and related species for actinide separation processes;
- inorganic complexes that can sequester heavy metal ions and then be used to form long-term storage media;
- detailed studies of the mechanism by which silicotitanates and related compounds react with cesium;
- rational design and synthesis of new crown ether compounds for potential use to remove cesium from solution; and
- use of iron-oxide-coated sand to remove strontium quantitatively from tank wastes.

Some nonradioactive materials need to be removed because they may cause problems with potential immobilization procedures. For example, nitrates can decompose at high temperatures to form gaseous products that may cause foaming in molten glass, and chromium and iron oxides can cause defects in glass waste forms. EMSP projects related to removal of these species include:

- a study of possible electrochemical oxidations of nitrates, nitrites, and organic species in tanks;
- explorations of the chemistry of chromium related to possible hydrothermal (supercritical water) and hydrogen peroxide oxidations for removal of chromium compounds from tank sludges; and
- a fundamental study of the chemical and magnetic properties of vitrification feed materials for possible applications of magnetic separation techniques.



Removal of Actinide and Lanthanide Species from Tank Waste
A project led by PNNL (54679) has prepared an actinide malonamide complex and determined the first crystal structure for such a complex.

PROBLEMS/SOLUTIONS

- Economically viable processing of high-level tank wastes requires selective removal of nonradioactive species from the wastes. Several EMSP projects are directed toward detailed studies of the chemical species present under tank conditions so that reliable separation procedures can be developed.
- Technetium is a particularly troublesome radioactive component of wastes because it tends to form ions that are mobile in groundwater, and vitrification processes may volatilize it. Development of stable inorganic complexes with technetium species may provide a route to not only separate it from other wastes but also convert it into forms suitable for long-term storage.

ANTICIPATED IMPACT

- The life-cycle cost for high-level waste remediation is estimated to be as high as $47 billion, so this is the area in which the greatest cost savings may be realized by investments in basic science and engineering technologies.
- Efficient separation of chromium from high-level waste sludge is a high-priority goal with a very high cost savings potential. The objective of an EMSP project is to lay the foundation for the application of hydrothermal processing for chromium separation from sludges.
- Radionuclides constitute less than one part in ten thousand in most high-level waste tanks, so efficient processes to separate these species from the remaining tank waste are essential to reduce the total volume of high-level waste to be stored. Without removal of cesium and strontium, for example, most of the 100 million gallons in underground storage tanks would require treatment as high-level waste. Even though several recent techniques for radionuclide removal are quite efficient, small improvements in this area could still have a large impact on the volume of waste that would need to be immobilized.

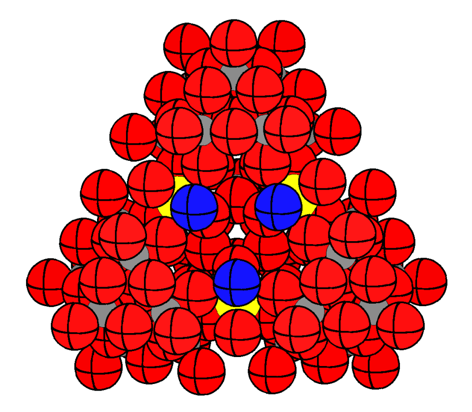
Removal of Actinide and Lanthanide Species from Tank Wastes

Techniques for the removal of actinides and other long-lived radionuclides are of interest to many waste treatment problems because efficient removal could result in large reductions in the volume of material that needs to be prepared for long-term storage. All separation procedures depend on the use of agents that can bind the radionuclides in forms that enable them to be removed from the rest of the waste materials. The DIAMEX and TRUEX processes use agents that contain amide groups for actinide separations processes, and a major EMSP project (54679), involving groups at PNNL and five universities, has focused on the fundamental science necessary for rational design of new complexing agents or ligands for actinide and lanthanide species. They have synthesized and characterized a variety of diamides and their complexes with metal ions, and their work has led to the design of several new molecules to be studied for possible application to actinide separations. They have also devised methods for measurements of the stability of the metal-ligand complexes, and they have carried out extensive theoretical computations to elucidate the factors that determine which ligands would be most useful for binding various radionuclides.

The Georgetown University/ORNL project (54716) has investigated possible uses of a class of inorganic compounds called polyoxometalates for removal of actinides and lanthanides from tank wastes. An example is a polytungstate with the formula $NaP_5W_{30}O_{110}^{14-}$ in which the sodium ion is in a cavity surrounded by phosphorous, tungsten, and oxygen atoms. Research in this project has shown that the central sodium ion can be exchanged for lanthanide (and presumably actinide) ions in the presence of high sodium concentrations without incorporation of iron or aluminum ions. In addition to the use of these compounds as sequestering agents, they also may be treated under relatively mild conditions to form cubic bronzes. These are very stable oxides of, for example, lanthanides and tungsten, and part of the project has been an exploration of these compounds as potential permanent waste forms (instead of glass or alternate ceramics). Explorations of compounds that could sequester technetium are also part of this project.

Removal of Cesium and Strontium from Tank Wastes

The radioactivity in underground storage tanks is mostly due to cesium-137 and strontium-90. The Texas A&M University/ORNL project (54735) has focused on development of highly selective inorganic ion exchangers for removal of cesium and strontium from tank waste and from groundwater; the Texas A&M work has concentrated on the synthesis and characterization of the materials, while the ORNL work has been directed toward preparing engineered forms of the powders as well as testing with actual nuclear waste solutions. Crystalline silicotitanate has been extensively studied as an ion exchanger for removal of cesium in tank wastes, and detailed studies of the mechanisms by which these and several families of other silicates function have been conducted. These studies involve "crystal engineering" by using various metal ions in the structures to make small changes in the crystal geometry, and these changes can result in major changes in selectivity for cesium or strontium removal from solution.



Removal of Actinide and Lanthanide Species
A Georgetown University project (54716) has synthesized a polyoxotungstate anion incorporating (yellow) uranium centers. Thermal treatment of the ammonium salt yields the inert tungsten bronze, U0.1WO3.

The design, synthesis, and characterization of improved crown ethers for metal-ion separations are the objectives of the ORNL/ANL/PNNL/University of Tennessee project (55087). The PNNL group has used molecular modeling techniques to attempt to understand the details of sodium or cesium ion binding in order to make suggestions for new compounds that should be investigated. The ORNL group has developed improved syntheses of some previously known crown ether compounds, and, guided by the PNNL work, they have prepared a new class of crown ethers with greatly improved cesium to potassium selectivity. The ANL group has explored rational designs of synergistic extraction systems for divalent metals, such as strontium, and they have investigated combinations of acids and crown ethers for solvent extraction systems. The University of Tennessee contribution has involved attempts to incorporate some of the new crown ethers into polymers to prepare resins for use with conventional packed-bed separation systems.

The objective of the University of Washington project (55146) is to develop methods to separate strontium and cesium from other high-level tank wastes in a form that allows them to be disposed of appropriately. Their work has emphasized the use of inorganic materials for the separations because they are not likely to generate new mixed waste disposal challenges. They have used iron-oxide-coated sand to remove strontium quantitatively from a simulated tank waste solution. Their approach to removal of cesium from simulated tank waste used an electrochemically controlled system with electrodes modified to provide for reversible capture of cesium, and they have investigated some fundamental properties of these electrodes to assess their potential for application in the Hanford tanks.

Removal of Organic Compounds from Tank Wastes

The organic compounds that are present in the underground storage tanks present unique problems, especially because they could cause safety and performance hazards when exposed to the high temperatures used for immobilization of inorganic wastes. The objective of a PNNL project (54996) was to explore the applicability of a novel use of gamma-radiation-induced catalytic destruction of organics on metal oxide particles. The idea was to generate electron-hole pairs in semiconductor particles using gamma irradiation, with redox reactions occurring on the surface of the particles. Experiments with titanium dioxide showed a modest improvement over a blank for reactions of EDTA, but smaller organics were not more reactive in the presence of the particles than without the particles present. Much of the work involved detailed studies of the role of surface defects in thermal and photochemical processes on model titanium dioxide surfaces. It was also found that an electron-hole mechanism on semiconductor surfaces is not responsible for decomposition reactions of tetraphenylborate, but rather the formation of benzene occurs by a thermal reaction in the presence of a metal-oxide-supported platinum catalyst as found by other workers at the Savannah River Site.

Removal of Anions from Tank Wastes

The anions in high-level waste tank supernate and saltcake are primarily nitrate, nitrite, and hydroxide. As described in a Tanks Focus Area Science Needs statement (S-WT-08-01), technologies to remove nitrate, nitrite, and several other anions are needed to enhance the efficiency of proposed vitrification processes. The California Institute of Technology/University of Wisconsin project (55137) is investigating possible electrochemical oxidations of nitrites, nitrates, and organic species in the tanks. The main focus of their efforts has been on the preparation and characterization of titania-coated metals for anodes, and they have shown that these corrosion-resistant materials show promise for the proposed remediation applications.

Removal of Chromium and Iron from Tank Wastes

According to a Site Technology Coordination Group Need Summary (RL-WT037-S), “our present level of understanding of the behavior of chromium compounds in tank-like environments and kinetic information under these conditions is virtually nonexistent.” The objective of a LANL project (54765) is to develop the scientific basis for hydrothermal separation of chromium from high-level waste sludges. Chromium hydroxide is the main chromium compound in these sludges, and detailed studies of the rates of dissolution were performed in this project. They found that oxidative dissolution could be accomplished at high temperatures with nitrate and at lower temperatures with oxygen, and they suggest that chromium can be rapidly dissolved from sludge using oxygen or air at temperatures slightly higher than current baseline sludge washing conditions.

The Furman University/LANL project (54828) has also investigated reactions of chromium hydroxide in basic solutions. Their efforts focused on the oxidative dissolution of chromium hydroxide that results from treatment with hydrogen peroxide, and they find that this rapid reaction is a promising method for treating Hanford tank wastes that have high chromium concentrations. Raman spectroscopy of these solutions was being used to study the identity of the actual reacting species in these reactions, and a high-pressure diamond-window cell was being constructed to study reactions under conditions necessary to produce supercritical water.

Some materials, such as iron oxides, can cause defects in glass that may reduce its usefulness as a storage medium for radionuclides. The ANL and coworkers project (55294) was designed to study both fundamental science and practical application issues related to use of magnetic separations of vitrification feed materials. They have characterized the chemical and magnetic properties of several candidate tank sludge and flyash materials, and they have developed hydrodynamic and electrodynamic models to explore the use of these properties to design optimal magnetic separation techniques. Although the flyash samples were found to have many submicron-sized particles that made them difficult to handle, high-gradient magnetic separations of tank surrogate samples were found to be useful. The design and testing of optimal conditions for open-gradient magnetic separations were underway.

Project Teams

Lead Principal Investigator (Award Number)

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  University of Alabama
  University of California – Berkeley
  University of New Mexico
  University of Oregon
- Georgetown University
  PI: Michael T. Pope (54716)
  Oak Ridge National Laboratory
- Texas A&M University
  PI: Abraham Clearfield (54735)
  Oak Ridge National Laboratory
- Los Alamos National Laboratory
  PI: Steven J. Buelow (54765)
- Furman University
  PI: Charles A. Arrington (54828)
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  PI: Michael A. Henderson (54996)
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  Argonne National Laboratory
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- California Institute of Technology
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