



INORGANIC AND ACTINIDE CHEMISTRY

INORGANIC CHEMISTRY IS AN IMPORTANT PART OF ALMOST ALL RADIONUCLIDE REMEDIATION PROCEDURES

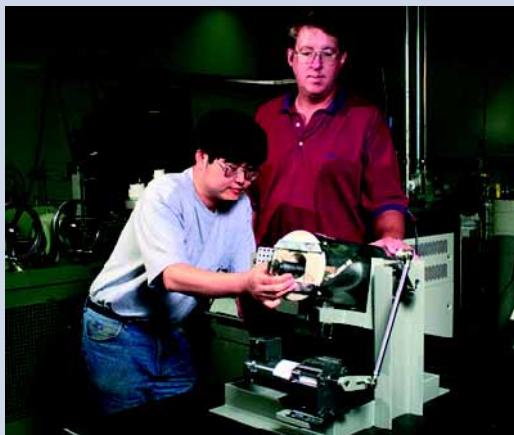
Chemistry at high temperatures and pressures is particularly relevant to the development of alternatives to incineration for waste remediation, and some EMSP projects in this area included studies of chemical processes in supercritical water and investigations of the chemistry of chromium compounds in supercritical water. Another project explored optimal conditions for remediation of organic compounds in water using ultrasonic irradiation.

Research related to the chemistry of metal ions in DOE wastes includes:

- Characterization of the chemical speciation of strontium, actinides, and other metal ions in the highly basic conditions found in high-level waste tanks.
- A study of the fundamental science necessary for the rational design of new ligands or complexing agents for separations of metal ions.
- The design of new polymeric agents for use in removing metal ions from solution by ultrafiltration.

The formation of gases in high-level waste tanks is of primary concern for tank safety. Two of the projects described below involved studies of the chemical reactions that result from the production of the initial products of radiolysis, while another explored non-radiolytic chemical mechanisms of gas formation in the complex mixtures found in high-level tanks.

The aggregation of colloidal particles can cause severe problems when pumping waste sludges through pipes, and one project focused on understanding the conditions necessary to avoid the formation of viscous gels during retrieval operations. The ideal products from the destruction of chlorinated hydrocarbons are inorganic chlorides and carbon dioxide, and an EMSP study explored reactions with metal oxides to form those products. Another project investigated methods for photoelectrochemical oxidations of hazardous organic materials.



Chemistry at High Temperatures and Pressures

Experiments by an ORNL project (55276) are designed to help determine optimum operating conditions for hydrothermal oxidation of aqueous mixed wastes. In this photo, scientists load uranium (VI) oxide samples into a rocking autoclave for solubility measurements at high temperatures.

PROBLEMS/SOLUTIONS

- Slurries of tank sludge materials can have very high viscosities with solid loadings in water as low as 1%, and such materials can clog transfer lines during waste retrieval. Fundamental studies of the agglomeration of the colloids that comprise the sludges may lead to chemical treatment methods that reduce the dilutions necessary to retrieve these materials.
- The chemistry of chromium compounds in the strongly basic conditions found in high-level tanks is not well understood. Two EMSP projects have not only examined the identity of the chemical species present under these conditions, but also have explored methods for removal of chromium compounds from sludges, as is desirable before immobilization.
- The removal of a particular radionuclide using complexing agents may be difficult to predict if the chemical species present in complex mixtures are not known. Several EMSP projects have examined the chemistry of metal ions under conditions similar to those in the tanks.

ANTICIPATED IMPACT

- Thousands of gallons of chlorinated hydrocarbons must be destroyed during remediation programs throughout the U.S. Department of Energy (DOE) complex, but incineration of these compounds is difficult. Basic research in the chemistry of metal oxides, oxidations in supercritical water, and the chemistry induced by ultrasonic irradiation may suggest practical alternatives to incineration.
- The life-cycle cost for high-level waste remediation has been estimated to be \$47 billion. Radionuclides comprise only a small fraction of the total mass of the high-level wastes, so small improvements in separation efficiencies could result in savings of millions of dollars.
- A large amount of low activity waste has been or will be immobilized in grout or sandstone. An EMSP project suggested that radiolysis of residual water in these media may actually be enhanced.

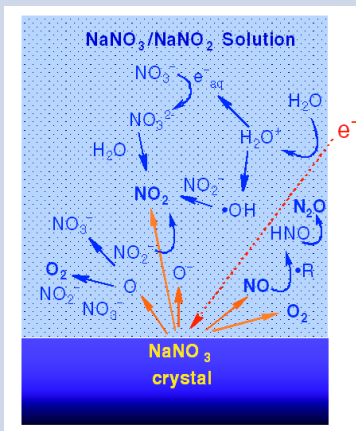
Chemistry at High Temperatures and Pressures

The University of Texas project (54506) has been directed toward fundamental understanding of the chemistry of species in supercritical water. They investigated the chemistry of aqueous nitric acid solutions at temperatures above 300°C and performed computer simulation studies of ion transport in water under extreme conditions. Carbonate/bicarbonate/carbonic acid equilibria were studied, and modeling and simulation studies of hydrolysis reactions in supercritical water have also been initiated.

The ORNL/University of Tennessee project (55276) has also investigated some fundamental chemistry and thermodynamics of hydrothermal oxidation processes. They have measured the pressure-volume-temperature relationships for high temperature and pressure mixtures of water, carbon dioxide, and nitrogen, and they have used molecular-level simulations to develop a predictive level of understanding of the chemical and physical properties of hydrothermal oxidation processes. They have also measured the solubility and speciation of uranium oxide and related carbonates in aqueous solutions at elevated temperatures, and they found that the solubility of UO_3 in a carbonate buffer decreased with increasing temperature due to the conversion of UO_3 to a polymeric species under these conditions.

A high-priority basic science need related to high-level waste is to understand the chemistry of chromium compounds in strongly basic solutions. A LANL project (54765) addressed this need with detailed studies of the rates of oxidative dissolution of chromium hydroxide at high temperatures and pressures with oxygen and nitrates, and a global kinetic model for the dissolution in alkaline solutions was developed. The effects of added organics and other metals on the rates have been studied. These studies determined the conditions necessary for chromium to be efficiently dissolved from high-level waste sludge using oxygen or air. They also examined the diffusion of inorganic nitrates in supercritical water and studied reactions of transuranic species under hydrothermal conditions.

A Furman University project (54828) was closely related to the LANL project described above. The rates of reaction of chromium hydroxide with hydrogen peroxide were studied in highly basic solutions, and they found that this reaction is a promising method for treating wastes that have high chromium concentrations. Raman spectroscopy was used to investigate the mechanism of this reaction, i.e., to investigate whether hydrogen peroxide or the hydroperoxide anion is the actual oxidizing agent in basic solutions. They also investigated reactions with chromium oxide, Cr_2O_3 , which is insoluble and unreactive with hydrogen peroxide at ordinary room temperatures.



Mechanisms of Gas Formation in High-Level Wastes

A PNNL project (54646) has shown that radiolysis of NaNO_3 crystals in aqueous solution produces NO_x radicals, O_2 , O , and O^- , which degrade organic complexants and initiate gas generation reactions.

When an ultrasonic field is applied to a liquid, small bubbles can be generated within the liquid with internal temperatures of thousands of degrees and pressures in excess of tens of kilobars. Thus, ultrasonic irradiation can destroy organic compounds without heating the bulk liquid to very high temperatures, and a University of Washington project (54897) has studied the fundamentals of acoustic cavitation and bubble dynamics in order to determine the optimal parameters to use for liquid-waste remediation. They used emission of light in the near-infrared region to investigate the nature of the microscopic bubbles and found that a sudden increase in the pressure above the solution results in a dramatic increase in light intensity that persists for several minutes. Emission spectra from sodium in solution was also observed, and this technique may be useful for alkali waste concentration monitoring.

Chemical Species Present in High-Level Waste

Studies of the chemistry of metal ions in highly basic media are of particular relevance to high-level wastes stored in tanks, and this is the subject of the University of New Mexico project (54595). The hydrolysis chemistry of a number of metal ions was

investigated in the presence of various anions that are typically present in waste media. The coordination chemistry of several new compounds was also explored for the purpose of developing new means to remove certain metal ions from otherwise stable oxide-hydroxide structures. This would be of particular importance to the goal of reducing the volume of material that needs to be treated as high-level waste.

The PNNL/Florida State project (54621) investigated the chemistry of strontium, americium, and curium under conditions similar to those in the high-level waste tanks. They have found that only a few organic complexing agents can affect strontium speciation under the highly basic conditions found in the tanks. The solubility for a trivalent actinide surrogate,

europium, was found to increase at highly basic conditions because of the formation of soluble hydrolysis species rather than the formation of metal-chelate complexes, and these studies are being used to develop processing strategies for selected tank wastes. Solution-phase calorimetry, determinations of osmotic coefficients, and capillary electrophoresis-mass spectrometry studies are also being used to improve fundamental understanding of chemical speciation under highly basic conditions similar to those in waste tanks.

Properties of Colloidal Agglomerates in Tank Sludges

The sludges in the Hanford tanks consist mostly of hydrated oxides of various metals along with insoluble phosphate salts. The PNNL/SNL/University of Washington project (54628) combined experimental and theoretical studies to determine the impact of colloidal agglomeration on tank waste processing. Particle size distributions, sedimentation behavior, and particle density data have been obtained on samples from several Hanford tanks, and sedimentation studies of well-characterized aluminum hydroxide particles were done to explore the factors affecting the agglomerate structures as well as to explore how chemical additives might be used to control sludge behavior. Detailed studies of how certain polymers function as steric stabilizers were also underway.

Mechanisms of Gas Formation in High-Level Wastes

The mechanisms of organic compound degradation and the routes to generation of hydrogen and other potentially troublesome gases are of primary concern for tank safety. The PNNL/University of Notre Dame project (54646) investigated some fundamental aspects of this problem by studying radiation effects at sodium nitrate (NaNO_3) crystal interfaces and in solutions of suspended oxide particles. They found that the direct products of NaNO_3 interfacial radiolysis are NO , O atoms, and O^- ions, which can undergo further reactions with organic compounds at the crystal surfaces in addition to producing NO_2 in aqueous solutions. Their studies of radiation effects in oxide particles have shown that yields of reducing radicals increase in the presence of small particles, and thus the radiolysis of residual water may actually be enhanced in grout or sandstone.

A closely related University of Notre Dame/PNNL (55229) project investigated the chemistry of nitrogen-oxygen species in waste tanks. They showed that most of the primary radicals produced by the irradiation of highly concentrated waste simulant solutions are rapidly converted to NO_2 or NO . They showed that NO_2 is the dominant species responsible for oxidation of organic compounds in DOE tank wastes. They also determined rate constants for reactions of organic radicals with nitrite ions, and they showed how these reactions may lead to the production of gases (H_2 and N_2O).

The primary focus of the Georgia Tech project (54807) was on chemical (non-radiolytic) mechanisms of gas formation in waste storage tanks. Earlier work had suggested that the anion NO^- was an important intermediate in the reaction of nitrite salts with organic complexing agents to produce nitrogen-containing gases. The synthesis of compounds that could be used to generate NO^- rapidly has been a continuing activity of this project; although some new synthetic procedures have been developed, detailed studies of NO^- chemistry had not yet been achieved. Other studies included the development of models for aluminum-catalyzed oxidation of an organic complexing agent by nitrite and an analysis of the relative contributions of thermal versus radiolytic pathways for decomposition of some organic complexing agents that are present in waste tanks.

PROJECT TEAMS

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- University of New Mexico
PI: Robert T. Paine (54595)
- Pacific Northwest National Laboratory
PI: Andrew R. Felmy (54621)
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PI: Thomas M. Orlando (54646)
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- Pacific Northwest National Laboratory
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University of New Mexico
University of Oregon
- Los Alamos National Laboratory
PI: Barbara F. Smith (54724)
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PI: Nathan S. Lewis (55137)
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- University of Notre Dame
PI: Dan Meisel (55229)
Pacific Northwest National Laboratory
- Oak Ridge National Laboratory
PI: John M. Simonson (55276)
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Design of New Agents for Metal Ion Separations

The discovery of molecules that form strong complexes with various metal ions has long been an important part of actinide and other heavy-metal chemistry. A major EMSP project (54679), involving groups at PNNL and five universities, focused on the fundamental science necessary for rational design of new complexing agents or ligands for actinide and lanthanide species. Their research included the synthesis and characterization of a number of diamides and their complexes with lanthanide metal ions, development of methods of measuring the binding affinities of the ligands for the various metals, and extensive theoretical modeling of the factors that govern the strength of diamide-metal interactions. They showed that small changes in the structure of a ligand can greatly alter the nature and strength of the metal-ligand interactions. Their work identified some new chemical structures that may provide improvements in separation technologies, and synthesis of these new compounds was underway.

If a water-soluble polymer binds the metal ions, then the metal ions can be removed from solution by passing the polymer-metal complex through a membrane filter that retains the polymer but not smaller species in solution. The investigators in the LANL/University of California – Davis/University of Massachusetts – Lowell project (54724) previously demonstrated this procedure for removing residual metal ions from electroplating solutions, for removal of plutonium and americium from waste waters, and for removal of mercury from processing equipment, for example. The EMSP project involved the use of combinatorial chemistry for synthesis and characterization of a large number of new metal-binding agents. Characteristics of the water-soluble polymers were determined, and rapid polymer assay techniques that can detect concentrations of metal ions as low as ten parts per billion were developed. In addition, new versions of ultrafiltration equipment were built and tested.

Electrochemically Based Remediation

One method of waste remediation is electrochemical oxidation, and the California Institute of Technology/University of Wisconsin project (55137) investigated new electrode materials for use in degradation of organic and nitrogen-containing compounds. Their primary focus was on the development of titania-coated anodes for photoelectrochemical oxidations. They showed that thin film sol-gel coatings of titania can provide some protection for metallic electrodes and that these materials show promise for remediation applications.

Reactions of Halogenated Organic Compounds with Metal Oxides

The reaction of metal oxides with chlorinated organic compounds to form metal chlorides and carbon dioxide has been proposed as a method for remediation of chlorinated hydrocarbons. A project at Texas A&M University (55115) involved detailed surface science studies of reactions of carbon tetrachloride and related molecules on several metal oxides in order to reveal the mechanism of the reactions. They also did a systematic study of the efficiency of the reaction on various metal oxides and found that the oxides with the highest basicity were the most reactive, i.e., barium oxide was more reactive than calcium oxide, for example, and sodium oxide was more reactive than barium oxide. Their work suggested that the addition of water to carbon tetrachloride that is reacted with barium oxide at high temperatures should result in the continuous formation of hydrogen chloride and carbon dioxide as reaction products.

FOR ADDITIONAL INFORMATION ABOUT THE EMSP, PLEASE CONTACT ONE OF THESE REPRESENTATIVES:

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