PNNL-13262

Science to Support DOE Site Cleanup: The Pacific Northwest National Laboratory Environmental Management Science Program Awards

Fiscal Year 2000 Mid-Year Progress Report

June 2000

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Pacific Northwest National Laboratory was awarded ten Environmental Management Science Program (EMSP) research grants in fiscal year 1996, six in fiscal year 1997, eight in fiscal year 1998, and seven in fiscal year 1999.(a) All of the fiscal year 1996 award projects have been completed and will publish final reports, so their annual updates will not be included in this document. This section summarizes how each of the currently funded grants addresses significant U.S. Department of Energy (DOE) cleanup issues, including those at the Hanford Site. The technical progress made to date in each of these research projects is addressed in more detail in the individual progress reports contained in this document.

This research performed at PNNL is focused primarily in four areas: Tank Waste Remediation, Decontamination and Decommissioning, Spent Nuclear Fuel and Nuclear Materials, and Soil and Groundwater Cleanup.

Tank Waste Remediation

One of the main problems facing DOE is the 350,000 cubic meters (92 million gallons) of mixed chemical and radioactive waste stored in more than 300 underground storage tanks at the Hanford Site (Washington), Oak Ridge Reservation (Tennessee), Savannah River Site (South Carolina), Idaho National Engineering and Environmental Laboratory (Idaho), and West Valley Site (New York). These tanks contain about 70% (720 million curies) of the man-made radioactivity existing in the DOE complex in the form of liquids, sludges, saltcake, and calcined solids (at Idaho). Remediation of this tank waste is one of the most technically complex, scientifically challenging, and potentially expensive problems facing DOE.

Hanford has 60% of the waste volume and 30% of the radioactivity for all DOE high-level waste tanks. At Hanford, 177 underground storage tanks contain 210,000 cubic meters (54 million gallons) of high-level waste. The current baseline approach to remediating this tank waste is to retrieve the waste and then separate the solids from the liquids. Once cesium, strontium, and other radionuclides are removed from the liquid, it will become a relatively low-activity stream that can be immobilized as low-level radioactive and chemical waste. The solid, high-activity stream will be pretreated to reduce its volume (mainly through the removal of nonradioactive inorganic components such as chromium, phosphorous, and aluminum) and then immobilized as high-level radioactive waste.

(a) PNNL Researchers are the lead principal investigators in these 25 projects. PNNL also collaborates with researchers at other institutions on 28 other EMSP projects. This document, however, does not include the annual reports for those collaborations, which are submitted through the lead institutions.

Safe Storage

Even safe storage of the waste in the tanks gives rise to technical issues. Chemical reactions in the tanks, including those caused by radiation and the slow corrosion of the steel tank walls, produce gases such as hydrogen, nitrogen, nitrous oxide, ammonia, and methane. Many of these gases are flammable, toxic, or both. In addition to generating gases, the reactions degrade organic compounds in the waste, change organic fuel and oxidant concentrations, and alter the surface chemistry of insoluble colloids, influencing sedimentation and gas/solid interactions. The EMSP project "**Mechanisms and Kinetics of Organic Aging in High-Level Nuclear Wastes**" is focused on understanding the radiolytic processes in these mixed-phase systems. The goals are to determine and understand the radiation-induced physical and chemical changes in the wastes and the rates at which they occur.

Most of the tanks have a layer of solids that can trap bubbles of generated gas. If too many bubbles become lodged in the solids layer it becomes buoyant, and the entire layer or pieces of it may rise to the surface and suddenly release the trapped gas. Other processes that disturb the waste may also release gas. Very large releases have the potential to create a flammable atmosphere in the headspace of a tank that, if ignited, could rupture the tank or filters in the ventilation system that control radionuclide release. Determining the amount of retained gas in the tanks is therefore a critical component of evaluating the safety hazard of the tanks.

Periodic, direct measurements of the gas volume in each tank would be very expensive and, in some cases, impossible. However, previous work has established that the waste level responds to barometric pressure changes, leading to a method for estimating the volume of retained gas. Interactions between the gas bubbles and the rheologically complex waste are poorly understood, though, causing inaccuracies in this method. The objective of the EMSP project "**Mechanics of Bubbles in Sludges and Slurries**" is to gain a fundamental understanding of these interactions and improve the accuracy of gas volume estimates.

Characterization

Characterizing the complex and heterogeneous wastes is difficult and expensive. Yet, an adequate characterization is vital to making decisions about each treatment and storage step. At Hanford, waste delivered to the pretreatment system must be demonstrated to be within certain specifications on composition, solids content, etc. Cost and final disposition of the high-level waste form will depend on the waste content of the immobilized product.

Retrieval and Waste Transfer

The wastes are complex and highly alkaline mixtures of many species, with sodium, nitrate, and hydroxide predominant. Some of the most interesting thermodynamics in the waste involve aluminum phases, which can precipitate or dissolve during waste processing depending on the waste's pH and the concentrations of certain ions. Changes in pH or waste composition during waste retrieval, transfer, and processing must be done thoughtfully to prevent unwanted precipitation or scale formation. Of all constituents of tank waste, aluminum species have the greatest potential for clogging pipes and transfer lines, fouling highly radioactive components such as ion exchangers, and shutting down processing operations. The primary focus of "**Dissolution, Precipitation, and Deposition of Aluminum-Containing Phases in Tank Wastes**" is to understand the major factors controlling precipitation, scale formation, and cementation of existing insoluble particles by aluminum-containing phases so that fouling and clogging can be avoided.

Pretreatment

Several EMSP projects are investigating innovative approaches in the area of separation processes. Radionuclides must be removed to prepare the liquid waste stream for immobilization as low-level waste, while nonradioactive species must be extracted from the high-activity waste stream to minimize its volume. Both aspects present a series of technical challenges.

Current strategies for reducing the volume of the solid, high-activity waste stream involve developing methods to selectively dissolve and remove nonradioactive elements such as aluminum, phosphorus, and chromium while retaining the radioactive elements in the sludges. The EMSP project "**Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes**" looks specifically at chromium, which is not removed effectively by current sludge washing techniques and is difficult to incorporate into glass. The project seeks to understand the speciation, dissolution, and redox reactions of chromium under conditions relevant to high-level waste, i.e., multicomponent, highly nonideal electrolyte systems. The project will provide critical data to support the development of pretreatment processes for the removal of chromium and thereby help to achieve major cost savings in high-level waste disposal.

Turning to the low-level waste stream, the removal of cesium appears to be straightforward, with ion-exchange technologies capable of meeting the performance criteria. In conventional ion-exchange processes, the cesium-bearing liquid passes through a reactor packed with an organic resin or other ion-exchange material. The cesium binds to the resin but not permanently. Once the resin has reached its cesium capacity, the cesium is flushed from the resin with acid and reused. However, this creates a second liquid waste stream that must be processed further (e.g., by incorporating into borosilicate glass) for long-term storage or disposal.

The EMSP project "**New Silicotitanate Waste Forms: Development and Characterization**" is investigating a new strategy for disposing of crystalline silicotitanate (CST) ion exchangers by in situ heat treatment with minimal or no additives to produce an alternative waste form. The CST is the most promising commercially available candidate for removal of cesium and strontium from tank wastes; however, it has been identified as a risk to vitrification due to its high level of TiO_2. This EMSP project is characterizing the phase relationships, structures, and thermodynamic and kinetic stabilities of CST waste forms and establishing a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry. This approach could significantly reduce the volume and costs associated with waste disposal, minimize the risk of environmental contamination during processing, eliminate problems associated with radiolytic hydrogen generation during short-term storage, and provide DOE with technical alternatives for waste disposal. Due to this work and other EM-50-funded projects, CSTs are being considered as one of three cesium-removal technologies at the Savannah River Site.

Self-assembled monolayers on mesoporous supports (SAMMS) is one such example of a new separation medium that could be applied to tank waste processing. A PNNL-developed technology, SAMMS sequesters heavy metals within small pores coated with a single molecular layer of ligands. The EMSP project "**Actinide-Specific Interfacial Chemistry of Monolayer Coated Mesoporous Ceramics**" is developing a SAMMS material to selectively bind actinides. These studies are aimed at understanding and optimizing the chemistry of the ligand monolayer and its interactions with the target actinide species.

Technetium is another radionuclide that causes regulatory concerns in the final waste forms. Technetium has a moderately long half-life and, if left in the immobilized low-activity waste, would soon become the dominant source of radioactivity. Removing technetium would therefore make the low-level waste form more benign. Technetium is also a relatively volatile material that is difficult to incorporate into glass under the high temperatures used in standard vitrification. However, technetium removal is complicated by its speciation in tank waste, one form of which is pertechnetate anion, TcO_4^-. While traditional ion exchange processes are quite effective on cations such as cesium and strontium, they are much less effective on anions. The EMSP project "**Electroactive Materials for Anion Separation B Technetium from Nitrate**" is investigating how to use electroactive materials to sorb technetium without also extracting nitrate anions, which are present in very high concentration. This new process expels (elutes) the technetium electrochemically rather than using a chemical eluant, reducing the amount of chemicals added and thereby minimizing waste. The research focuses on manipulating specific properties of redox polymers to control their reversibility, selectivity, stability, intercalation/de-intercalation rates, and capacity.

Immobilization

Once the high-activity stream has been reduced in volume, the remaining waste, with its concentrated radionuclides, will be immobilized. The approach DOE has chosen for most of its sites is to vitrify the waste, that is, to incorporate it into glass. With DOE support, large electrically heated melters have been developed for waste processing. However, a number of scientific issues remain that could affect melter operation and the amount of waste that can be incorporated into the glass without reducing its durability. The EMSP project "**Modeling of Spinel Settling in Waste Glass Melter**" studies the formation and settling of spinel, the most common crystalline phase that precipitates in molten high-level waste glass. Spinel is a product of an interaction between Cr_2O_3, Fe_2O_3, NiO, FeO, and other oxides that are components of virtually all high-level waste streams at Hanford and Savannah River. Spinel formation in a high-level waste melter limits the waste fraction in glass because accumulation of spinel interferes with melter operation and shortens its lifetime. Understanding and preventing spinel formation will therefore enable higher waste loading, reducing the costs of high-level waste disposal potentially by billions of dollars.

Storage and Disposal

Once immobilized, the low-activity waste will be disposed on site, while the high-activity waste is to be disposed at the federal geologic repository. However, interactions between alkali ions (such as sodium) and radionuclides in the immobilized waste that could affect their release rate are not well understood. The impact of internal radiation on the long-term performance of these immobilized forms is also unclear. And, given the time frames involved (ca. 10,000 years) the data will not be gathered from simple experimentation. The EMSP project "**Ion Exchange Processes and Mechanisms in Glasses**" investigates ion exchange reactions and kinetics within the glass and relates those kinetics to glass structural properties. The understanding and associated data from this project has shown that the baseline formulation for low-level waste (LLW) glass will not meet regulatory leaching requirements for long-term disposal. In addition to this initial evaluation, these data have been used to reformulate the LLW glass to provide a final product that will retain the radionuclides of interest within the regulatory limits. It is also important to note that these studies will benefit the assessment of waste forms proposed for the immobilization and disposal of plutonium residues and scrap and excess weapons plutonium.

Decontamination and Decommissioning

DOE built thousands of facilities to generate and process nuclear weapons material. Part of the cleanup agenda involves closing the buildings themselves (e.g., nuclear reactors, chemical processing facilities, and reactor fuel pools) after characterizing, dismantling, and cleaning out facilities within them (e.g., glove boxes and hot cells). Radioactive contamination must often be cleaned from surfaces in these facilities to close ("decommission") them. Contamination may be physically removed by wiping, scraping, or scabbling, or it may be washed off using special cleaning agents. Virtually every DOE site has facilities awaiting or undergoing decontamination and decommissioning, and the major sites may have hundreds.

Two PNNL EMSP projects are focused on understanding and improving the methods used for cleaning surfaces. "**Microbially Promoted Solubilization of Steel Corrosion Products and Fate of Associated Actinides**" probes some of the fundamental scientific issues regarding a microbial process with potential for decontaminating corroding metal surfaces. Certain iron-reducing bacteria can dissolve the rust and oxide layers on steel and thereby release radionuclide contaminants attached to those surfaces. The actinides are sorbed by cell surfaces or precipitated within biofilms that can be removed and recovered by an enzymatic digestion of the microbes. This environmentally benign, enzymatic process avoids the use of hazardous or toxic chemicals and minimizes the volume and toxicity of secondary wastes. Similarly, "**Contaminant-Organic Complexes, Their Structure and Energetics in Surface Decontaminant Processes**" investigates the use of powerful, microbially produced chelates (called siderophores) as decontamination and sequestering agents. Studies of these compounds demonstrate that their binding affinity for iron and actinides with a (IV) valence state are as much as 20 orders of magnitude higher than other chelating agents (i.e., EDTA).

Spent Nuclear Fuel and Nuclear Materials

Another legacy of nuclear weapon production is spent nuclear fuel, plutonium residues, and scrap and excess weapons plutonium. DOE has 2500 metric tons of spent nuclear fuel (SNF) in water storage across the complex. For example, the Hanford Site K-Basins hold 2100 metric tons of spent fuel, much of it severely corroded. Similar situations exist elsewhere in the DOE complex, especially at Savannah River and Idaho National Engineering and Environmental Laboratory. DOE plans to remove much of this fuel and seal it in canisters for "dry" interim storage for up to 75 years awaiting permanent disposition. However, chemically bound water will remain in cracks and bound to surfaces even after proposed drying steps, leading to possible long-term corrosion of the containers and/or fuel rods themselves, radiolytic generation of H_2 and O_2 gas, which could lead to deflagration or detonation, and reactions of pyrophoric uranium hydrides. No thoroughly tested model is currently available to predict fuel behavior during preprocessing, processing, or storage. The EMSP project "**Radiolytic and Thermal Process Relevant to Dry Storage of Spent Nuclear Fuels**" is therefore studying the radiolytic reactions, "drying" processes, and corrosion behavior of actual SNF materials and pure and mixed-phase samples. These studies have shown the effect of radiolysis of water adsorbed on or in hydrates or hydroxides, thermodynamics of interfacial phases, and kinetics of drying. This work has direct applicability to the Hanford K-Basins fuels and will also be useful in evaluating transportation and storage issues at Yucca Mountain in DOE's Office of Civilian Radioactive Waste Management.

Dried and packaged SNF will ultimately be shipped to the federal geologic repository for final disposal, while transuranic materials such as plutonium and uranium will be treated (if necessary), packaged, and shipped to the Waste Isolation Pilot Plant near Carlsbad, New Mexico. The EMSP project "**Distribution and Solubility of Radionuclides and Neutron Absorbers in Waste Forms for Disposition of Plutonium Ash and Scraps, Excess Plutonium, and Miscellaneous Spent Nuclear Fuels**" is working to understand the distributions, solubilities, and releases of radionuclides and neutron absorbers in these materials after disposition. The results will provide the underpinning knowledge for developing, evaluating, selecting, and matching waste forms for safe disposal and for developing models of their long-term performance. The main progress has occurred on silicate systems and will be useful in predictive capabilities for glass waste farms.

Soil and Groundwater Cleanup

Contaminant plumes, contaminated soils, and landfills account for some 4,800 waste sites on DOE property in 31 states. Approximately 35 million cubic meters of soil are contaminated with low-level and mixed low-level waste. Another 1.2 million cubic meters of soil is contaminated with transuranic and mixed transuranic waste. Landfills of buried waste are estimated to contain 3 million cubic meters of low-level waste. This includes 105,000 cubic meters of retrievably stored transuranic waste. Several hundred square miles of groundwater are contaminated with a variety of radionuclides and hazardous chemicals in concentrations above drinking water standards and DOE's concentration guidelines. At Hanford alone there are nearly 150 square miles of groundwater contamination. The radioactive and hazardous wastes are dispersed through large volumes of soil and groundwater, making potential treatment by conventional soil excavation and groundwater cleanup technologies ineffective and costly. In addition, some 650,000 metric tons of solid waste is buried at Hanford.

In 1997, part of the call was designed to help the project fill many of the gaps in knowledge through EMSP. The current baseline approach for treating contaminated groundwaters is to pump out the groundwater, treat it ex situ, and return it to the subsurface ("pump and treat"). For contaminated soils, the plan is simple: dig it up and dispose of it in a controlled disposal unit. At Hanford, that unit is the Environmental Restoration Disposal Facility (ERDF).

ERDF, centrally located on the 200 Area plateau, is receiving contaminated soils and solid waste from the 100 Area. Two cells are now operating with a capacity of approximately 1.2 million cubic yards each. The potential exists for eight new cells depending upon future needs. These cells, classified as RCRA (Resource Conservation and Recovery Act) landfills, have a design life of approximately 20–30 years, which may be extended through the use of caps and/or engineered barriers.

While ex situ options may be available and effective over the short term, they are more expensive, labor intensive, and have a greater potential for worker and environmental risk than in situ methods. Consequently, there are many drivers for the development of in situ treatment, monitoring, and characterization solutions.

One area where there was an identified knowledge gap at Hanford was the rate of migration of radioactive cesium and other contaminants in the subsurface from tank leakage or waste cribs. Although it is strongly sorbed by the micaceous fraction of the soil, cesium appears to be moving faster towards the groundwater and, ultimately, the Columbia River than previously thought possible. Two EMSP projects are focused on understanding contaminant fate and transport. The EMSP project "**Mineral Surface Processes Responsible for the Decreased Retardation (or Enhanced Mobilization) of ^{137}Cs from High-Level Waste Tank Discharges**" is investigating the geochemistry of cesium ion adsorption under conditions appropriate to high-level waste tank releases. This work has shown that high sodium concentrations in tank waste suppress all but the most selective cesium sorption sites on the frayed edges of micaceous particles and that the cesium migration depth is strongly controlled by the sodium concentration. The hydroxide and aluminate compounds in high-level waste may alter these sites chemically, leading to faster transport through the soil.

Previous attempts to predict vadose zone transport have neglected driving forces and mechanisms of nonuniform contaminant migration, which result in erratic flow patterns and cause contaminants to bypass much of the unsaturated soil matrix. The primary objective of "**Rapid Migration of Radionuclides Leaked from High-Level Waste Tanks: A Study of Salinity Gradients, Wetted Path Geometry, and Water Vapor Transport**" is to investigate the causes and extent of nonuniform flow in the vadose zone and its effects on the migration of contaminants leaked from single-shell tanks. These driving forces include the effect of elevated surface tension of highly saline fluids on wetting front instability, finger formation, and contaminant mobility and osmotically driven vapor flux. The project will incorporate its findings into an existing DOE-developed numerical simulator to improve predictions of contaminant migration.

In fiscal year 1998, the Groundwater Vadose Zone (GW/VZ) integrated project was initiated to bring all of the issues that affect contamination of the soils and groundwater at the Hanford Site under one program. To begin the process, a roadmap was developed to determine the underlying gaps in knowledge that was needed to solve the problems associated with the contamination. As a result of this roadmapping effort, the EMSP program agreed to allow the GW/VZ project assist in the preparation of the call for proposals in 1999, focusing the call on the problems identified with the roadmap. The EMSP projects awarded fell into three categories: 1) waste/sediment interactions and process modeling, 2) vadose zone field studies, advanced monitoring, and transport modeling, and 3) dense non-aqueous phase liquid (DNAPL) monitoring and remediation.

In the first category, waste/sediment interactions and process modeling, the goal of the research is to determine how the waste interacts with the soils, resulting in models to predict the holdup and release of contaminants. The surfaces of the minerals will interact with the contaminants, depending on the nature of the surfaces. The project "**Technetium Attenuation in the Vadose Zone: Role of Mineral Interactions**" is looking at the role of divalent iron-containing minerals in the reduction/precipitation of technetium in the environment. In addition to the initial reactions, the project will determine the stability of the precipitates to find out if natural attenuation in the soils will decrease the mobility of technetium, resulting in the potential savings in the cleanup. Another project looking into the reactions of surfaces is "**The Influence of Calcium Carbonate Grain Coatings on Contaminant Reactivity in Vadose Zone Sediments.**" This project is looking into how calcium carbonate on the surface of minerals will affect the interactions between soil particles and the contaminants. Carbonates will enhance the sorption of some contaminants (e.g., strontium-90 and cobalt-60) but may interfere with the interaction between the minerals and the species that will undergo reduction reactions (e.g., chromate and pertechnetate). Because many of the minerals in the soil are silicates, one of the concerns is how silicates dissolved by the leaking of the basic tank wastes into the subsurface will interact with some of the radionulides, potentially complexing them and increasing their mobility. The project titled "**The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica Species to High Concentration: Effects on Neutralization of Leaked Tank Wastes and Migration of Radionuclides in the Subsurface**" will examine the effect these dissolved silicates have on contaminant mobility.

In addition to the minerals providing surfaces for oxidation/reduction reactions, one of the potential remediation technologies is to introduce a reductant into the environment to react with contaminants, resulting in immobilization of some of the contaminants of concern. DOE has been testing a process called In Situ Gaseous Reduction (ISGR) where the hydrogen sulfide is added to contaminant plume to convert it into a non-mobile and/or non-hazardous form. An understanding of the kinetics and mechanisms of interaction of the reductant with the contaminants and surrounding minerals will be addressed in the project titled "**Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone,**" which PNNL co-leads with the New Mexico Institute of Mining and Technology.

The second category of the projects supporting the GW/VZ project is the vadose zone field studies, advanced monitoring, and transport modeling. This work is mainly focused on looking at transport phenomena in actual field settings and the delineation of the contamination within the vadose zone. At the Hanford Site, there are numerous natural formations within the sediments that may restrict the transport of contaminants or may provide preferential pathways the enhance the movement of the contaminants. The project "**Influence of Clastic Dikes on Vertical Migration of Contaminants in the Vadose Zone at Hanford**" will look at the effect of the naturally occurring clastic dikes in the vadose zone on flow to better understand the fate and transport of contaminants at the 200 West Hanford Tank Farms. In a more general treatment of the transport of contaminants, the project "**Quantifying Vadose Zone Flow and Transport Uncertainties Using a Unified, Hierarchical Approach**" will look at parameterizing models of flow and transport in the heterogeneous vadose zone. This project will allow the elucidation of relationships between the quantity and spatial extent of characterization data and the accuracy and uncertainty of flow and transport predictions. Another important aspect in understanding the flow and transport of contaminants in the subsurface is the ability to delineate the contaminant plumes and identify the specific contaminants. At the Hanford Site, the species of most concern are radionuclides. The project "**Radionuclide Sensors for Water Monitoring**" will look at chemistries for selective preconcentration/separation directly on or within the area of a radioactivity detector. The work will involve looking at new materials and processes that can then be incorporated into field-deployable sensors.

The final area of study in the GW/VZ project includes monitoring and remediation of DNAPLs, which are still a major problem for many governmental agencies and private industries, including DOE. Among the planned remediation technologies for these organic materials, in situ bioremediation offers advantages over physical treatments (e.g., pump and treat systems) due to the potential reduction in schedule, cost, public acceptance and the final achievable cleanup levels. However, this approach still has many uncertainties, such as the feasibility of this process on recalcitrant contaminants in deep vadose zones where microbial populations are low and discontinuous and how hydrologic features of the vadose zone control microbial processes. The project "**Integrated Field, Laboratory, and Modeling Studies to Determine the Effects of Linked Microbial and Physical Spatial Heterogeneity on Engineered Vadose Zone Bioremediation**" will provide an increased understanding of the effect of interacting hydrologic and microbiological processes that control the feasibility of engineered bioremediation of chlorinated compounds in the vadose zone.

Health Effects

In 1999, EMSP teamed with the Low Dose Radiation Research Program in DOE's Office of Biological and Environmental Research to support research to determine whether low dose and low dose-rate radiation presents a health risk to people that is the same as or greater than the health risk resulting from the oxidative by-products of normal physiological processes. This information is an important determinant in decisions that are made to protect people from adverse health risks from exposure to radiation.

Extensive research on the health effects of radiation using standard epidemiological and toxicological approaches has been used for decades to characterize responses of populations and individuals to high radiation doses and to set exposure standards to protect both the public and the workforce. These standards were set using modeling approaches to extrapolate from the cancers observed following exposure to high doses of radiation to predicted but unmeasurable changes in cancer frequency at low radiation doses. The use of models was necessary because of our inability to detect changes in cancer incidence following low doses of radiation. Historically, the predominant approach has been the Linear No Threshold model that assumes each unit of radiation, no matter how small, can cause cancer. As a result, radiation-induced cancers are predicted from low doses of radiation for which it has not been possible to directly demonstrate cancer induction.

One PNNL project, "**Linking Molecular Events to Cellular Responses at Low Dose Exposures,**" is looking into defining thresholds in cell-signaling pathways that are required for cellular transformation and that may be targeted by low-dose radiation. This information could be used to demonstrate nonlinear relationships between low-dose radiation and cancer.

The second PNNL low-dose project, "**Sensitivity to Radiation-Induced Cancer in Hemochromatosis,**" will perform studies with mice to determine the sensitivity to low doses of radiation and the effect of iron on this sensitivity. Researchers will then correlate increases in sensitivity with changes in insulin-related signaling in the tumors and normal tissue in the target organs. This work will lead to performing additional studies to determine the thresholds in dose-response relationships, allowing us to determine excess risk with low doses of radiation in human populations under EPA's draft Cancer Risk Assessment Guidelines.

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Tank Waste Remediation

Mechanisms and Kinetics of Organic Aging in High-Level Wastes

(Project Number: 65408)

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Problem Addressed

Concerns have arisen about the organic chemicals in highly radioactive wastes stored at the Hanford and Savannah River DOE sites. The organic chemicals, including complexants, are so energy-rich that their presence in nitrate-rich wastes is a potential safety issue. The organic chemicals degrade by radiolytic and thermal pathways to a wide range of species, including flammable and toxic gases (H_2, N_2, NH_3, and organic vapors) that also pose safety hazards. Organic complexants interfere with removal of radionuclides during pretreatment to produce low-level waste feed to treatment facilities. The reducing characteristics of organic chemicals change the oxidation states of metal ions, altering metal ion solubility and adversely affecting pretreatment goals. Also, knowledge of the organic degradation products likely to be present in wastes is needed to develop analytical methods that address DOE and regulatory agency requirements for water.

Research Objective

The objective of this research is to develop a basic understanding of organic degradation reactions that occur in high-level-waste (HLW) and to assemble models that describe the rates and products of degradations. Emphasis is placed on the reactions of complexants and their associated degradation products.

Research Progress and Implications

This report summarizes progress after 1.5 years of a three-year project. Our work investigates 1) reactions that initiate by or originate from radiation effects, 2) studies of thermally activated reactions that occur in the absence of radiation, and 3) use of computational methods to characterize reaction intermediates. Information obtained has been instrumental in closing tank safety issues at the Hanford Site.

The study of radiation-induced organic degradation is closely coordinated with other EMSP projects that work to understand radiation effects in homogeneous solutions ("The NO_x System in Nuclear Waste," D. Meisel, P.I.) and at interfaces with oxides and solid sodium nitrate ("Interfacial Radiolysis Effects in Waste Tank Characterization," T. Orlando, P.I.). These projects show that the high concentrations of sodium nitrate and nitrite in HLW ultimately cause radiation from radionuclide decay to generate NO_x radicals. Because little is known of the reactions of NO_2 with organic chemicals in HLW, the work focuses on elucidating these reactions. Products and rates of reactions are measured by contacting NO_2 with aqueous solutions containing organic solutes. From the products and analogies to related systems, reaction mechanisms are inferred and quantitative kinetic models constructed.

Of the major complexants used in Hanford nuclear materials processing, only HEDTA and glycolate are readily oxidized by thermal reactions to give flammable gases. Nitrite ion supplies the oxidizing equivalents, while aluminate ion or other aluminum species is a catalyst. Prior investigations proposed that aluminate ion catalyzes the nitrosation of alcohol functional groups in glycolate and HEDTA. The so-formed organic nitrite ester then degrades yielding precursors to H_2, N_2O, and NH_3. Recent tests conducted by this project contradict this mechanism. The rates of saponification of EtONO (a model for HEDTA) and nitritoacetate (nitrite ester of glycolate ion) were measured in the absence and presence of aluminate ion, and no enhancement of rate was observed with aluminate. If aluminate catalyzes formation of RONO from nitrite ion and ROH, it should catalyze the reverse reaction, i.e., saponification of RONO. Therefore, alternative mechanisms are required to explain and ultimately predict the thermal reaction kinetics. One such mechanism under consideration suggests that aluminum ion binds both ROH and nitrite ion, thereby fostering intramolecular hydrogen transfer and electron transfer reactions.

Solution properties of organic intermediates are being characterized by theoretical methods in collaboration with computational chemists at PNNL and the Notre Dame Radiation Laboratory. Computational methods complement experimental measurements, guide future experiment, and provide thermochemical data that cannot be easily measured. The initial work is evaluating newly developed quantum-mechanical dielectric-continuum models for characterizing solvated radicals, ions, and zwitterions relevant to organic tank chemistry.

Planned Activities

Work will continue on these efforts. Rates and products of NO_2 reacting with larger organic structures in alkaline solutions will be measured and the data incorporated into predictive kinetic models. The investigation of thermally initiated, aluminum-catalyzed oxidations will shift focus to testing new mechanisms for oxidation of glycolate, HEDTA, and related structures. Computational work will survey the ability of solvation models to reproduce solution properties of 1- and 2-carbon systems. If satisfaction is obtained from available methods, calculations will extend to the relevant polyfunctional systems.

Information Access

1999 Progress Report: http://apollo.osti.gov/em52/1999projsum/65408.pdf

Fessenden R, D Meisel, and DM Camaioni. 2000. “Addition of oxide radical ions (O^-) to nitrite and of oxide ions (O^{2-}) to nitrogen dioxide.” *J. Am. Chem. Soc*. (in press).

Meisel D, DM Camaioni, and TM Orlando. 2000. “Radiation and chemistry in nuclear waste: The NO_x and organic aging.” *First Accomplishments of the Environmental Management Science Program, ACS. Symp. Series*, PG Eller and W Heineman, eds. (in press).

Camaioni DM and ST Autrey. 2000. “Thermochemical kinetic analysis of mechanism for thermal oxidation of organic complexants in high level wastes.” *First Accomplishments of the Environmental Management Science Program, ACS. Symp. Series*, PG Eller and W Heineman, eds. (in press).

Mechanics of Bubbles in Sludges and Slurries

(Project Number: 60451)

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Research Objective

Previous studies have established that the waste level in Hanford tanks responds to barometric pressure changes, the compressibility of retained bubbles accounts for the level changes, and the volume of retained gas can be determined from the measured waste level and barometric pressure changes. However, interactions between the gas bubbles and rheologically complex waste cause inaccurate retained gas estimates and are not well understood. Because the retained gas is typically a flammable mixture of hydrogen, ammonia, and nitrous oxide, accurate determination of the retained gas volume is a critical component for establishing the safety hazard of the tanks. Accurate estimates of retained gas from level/pressure data are highly desirable because direct in situ measurements are very expensive in an individual tank and impossible in many single-shell tanks.

The objective of this research project is to gain a fundamental understanding of the interactions between gas bubbles and tank waste during barometric pressure fluctuations. It is expected that elucidation of the bubble/waste interaction mechanisms will lead to the development of models for a more accurate determination of gas content in Hanford tanks, waste properties from level/pressure data, and the effect that barometric pressure fluctuations have on the slow release of bubbles. The results of this research will support critical operations at the Hanford Site that are associated with the flammable gas safety hazard and future waste operations such as salt-well pumping, waste transfers, and sluicing/retrieval.

Research Progress and Implications

This report summarizes work done in 2.5 years of a three-year project. Progress has been made in each area of modeling bubble behavior in continuum materials (sludges), from both solid mechanics and fluid mechanics viewpoints, modeling studies of compressible bubbles in particulate materials (slurries), and experimental studies of bubbles in both sludges and slurries.

Experiments have quantified the effects of small pressure changes on bubble volumes in simulated waste. In single- and multiple-bubble experiments, a fluid of known rheological properties fills an apparatus attached to a pressure regulation system. As step changes or cycles of pressure are made, level changes are tracked. For single bubbles, cameras capture bubble shape changes as well as level changes in a capillary tube standing over the vessel. For multiple-bubble experiments, the level is measured by the same gauge used in the Hanford tanks. Experiments have been performed on both water-based and oil-based simulants, but each has limitations. The data show hysteresis, where the level depends on the pressure history in addition to the current pressure, indicating that some stresses must be overcome before the bubble volume responds.

A general procedure was developed to find the stress and strain fields produced by periodic pressure variations for a spherical bubble in an elastic-plastic medium, where the gas inside the bubble is considered soluble in the medium. For a given set of parameters, the bubble volume was computed as a function of applied pressure and solubility coefficient. Residual stresses are originated by plastic deformations that occur during the expansion or compression of the bubble.

The current model is significantly more rigorous than those of previous studies at PNNL and has yielded significant new results. New estimates of material strength based on the model are an order of magnitude smaller than previous calculations that accounted poorly for elastic and plastic regions and residual stresses. Results show that increasing the waste strength causes an increasing hysteresis in the relationship between bubble radius and pressure. This occurs because the waste, which is a soft solid, resists the expansion and compression of the bubble. In addition, the hysteresis depends on Young's Modulus. It was also found that the pressure cycles are not symmetric and that the whole loop may be markedly curved.

This model enables the engineer to estimate the rate at which bubbles rise through the sludge as a function of the specific barometric pressure history. Within the model assumptions, bubble rise takes place as long as the magnitude of the pressure fluctuations (regardless of whether the medium is compressed or decompressed) exceeds the yield condition for the material. Work to gain a better understanding of the interplay among the various parameters and the feasibility of estimating mechanical properties continues.

From the fluid mechanics point of view, as a bubble expands under the influence of gravity and changing barometric pressure, the yield stress of the surrounding fluid is eventually overcome, its structure collapses, and the bubble rises within the yielded region. As the bubble grows, the yielded region grows and interacts with the yielded regions of nearby bubbles. In a fully connected, yielded region, bubbles move about, coalesce, and rise. How this interaction occurs and what happens when the yielded regions intersect is the heart of the problem. The project team is most interested in determining which regions are yielded (act like viscous liquids) and which are unyielded (act like solids).

The mechanics of bubble movement in slurries representative of Hanford tank wastes are more appropriately modeled as porous media. A one-dimensional biconical-pore-network model is being applied to determine the effective compressibility of the gas in the slurry. This information is important for calculating the volume of gas in the slurry from changes in waste level produced by fluctuations in barometric pressure.

The compressibility of the gas is a function of its pressure, which is the sum of barometric pressure, the known hydrostatic pressure from the liquid in the tank, and capillary pressure in the porous medium formed by the slurry. Three time scales are involved. Over a period of months or years, chemical reactions in stored liquid waste create volatile components that diffuse to and accumulate in bubbles. Bubble mass and volume increase slowly at fixed liquid pressure, determining the initial states of bubbles when barometric pressure changes. On a time scale of hours, bubble volume responds to changes in barometric pressure. On this time scale, effective compressibility is observed.

On a shorter time scale, seconds or less, interfaces between the viscous liquid and bubble advance or retreat impulsively, driven by capillary forces. For expanding bubbles, whether due to accumulation of mass over a period of months or to a short-term decrease in barometric pressure, impulsive jumps occur from the throat of one pore to near the throat of the next. During pressure *increases*, however, interfaces jump from pore *body* to pore body. Because most jumps in tank waste have occurred during the slow growth of bubbles over months, most bubbles are lodged at pore throats, ready to jump again if pressure decreases. However, these same bubbles do *not* jump backward if pressure increases, until their interfaces first retreat to pore bodies. Thus, a population of bubbles has a significantly higher effective compressibility during decreasing pressure than during increasing pressure.

The project's constricted-tube model can fit tank data with level-pressure hysteresis, but ambiguity remains on the relationship between bubble geometry and capillary pressure. The PNNL experiments or other threads of the project may provide the information needed to solve that problem.

Planned Activities

For the remaining seven months of this project, the parametric study on the multiple pressure cycles will be extended. In addition, the effect of neighboring bubbles (multi-bubble problem) on the plastic and elastic deformations will be assessed. The numerical simulations of a bubble moving in a viscoplastic fluid will focus on the calculation of the topology of the yielded regions. Further multiple-bubble experiments will be performed and compared with the modeling results to reconcile the differences between the observed behavior and the different modeling approaches.

Information Access

Gauglitz PA, G Terrones, DP Mendoza, and CL Aardahl. 2000. "Behavior of flammable gas bubbles in Hanford high-level waste." *Proceedings of Waste Management 2000*, Tucson, Arizona.

Gauglitz PA, G Terrones, DP Mendoza, and CL Aardahl. October 1999. "Elastic-plastic deformation of a soft solid by an expanding bubble." The Society of Rheology 71st Annual Meeting, Madison, Wisconsin.

Gauglitz PA, G Terrones, CL Aardahl, DP Mendoza, and LA Mahoney. March 1999. *Mechanics of bubbles in sludges and slurries: Experimental studies and solid mechanics modeling results*. Engineering Foundation Conference on Rheology in the Minerals Industry II, Oahu, Hawaii.

Denn MM and G Marrucci. “Squeeze flow between finite plates.” *J. Non-Newtonian Fluid Mechanics* (submitted).

Kam SI and WR Rossen. “Anomalous capillary pressure, stress and stability of solids-coated bubbles.” *J. Colloid Interface Sci.* (in press).

Gauglitz PA, G Terrones, DP Mendoza, MM Denn, SJ Muller, and WR Rossen. June 1998. “Mechanics of bubbles in sludges and slurries: Initial progress.” Hanford Technical Exchange, Richland, Washington.

Gauglitz PA and JH Konynenbelt. November 1997. “Mechanics of bubbles in sludges and slurries: Preliminary experiments.” Fluid Mechanics Poster Session, AIChE Annual Meeting, Los Angeles, California.

Dissolution, Precipitation, and Deposition of Aluminum-Containing Phases in Tank Wastes

(Project Number: 65411)

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Research Objective

The goal of the proposed work is to understand the kinetics of dissolution, precipitation, and scale formation involving aluminum-containing phases in alkaline salt solutions representative of tank wastes. This research will identify aluminum-containing phases that are likely be present or to form and will predict conditions under which such phases are likely to form or be present. Experiments will identify processing conditions that either promote or inhibit the heterogeneous or homogeneous nucleation and growth of aluminum-containing phases to form precipitates or scales. Test conditions encompass conditions anticipated for waste storage, washing, leaching, concentration in evaporators, and contact with pipes, ion exchangers, and other processing media.

Research Progress and Implications

Aluminum is one of the principal elements in alkaline nuclear wastes stored at DOE sites, including Hanford and Savannah River. Two of most widely observed phases are gibbsite and boehmite. From the viewpoint of tank waste processing, the dissolution kinetics of gibbsite and boehmite are different, and the slow dissolution phase, boehmite, is more of a concern than gibbsite. It is important to understand when and under what conditions gibbsite and boehmite form in the tank waste and how easy it is for the gibbsite to transform into boehmite.

The hydrothermal stability of gibbsite and boehmite was studied in alkaline solutions (2 or 3 M NaOH). The following conclusions have been reached:

- Boehmite is always the stable phase. Gibbsite tends to transform to boehmite.

- Two fundamental mechanisms were identified for hydrothermal transformation of gibbsite to boehmite:

  - Dissolution of gibbsite and precipitation of boehmite in the solution. The dissolution and precipitation occurred when the reaction was carried out in a sealed container. Gibbsite was dissolved along (001) planes. Boehmite nucleated from the solution. Further dissolution of gibbsite and growth of boehmite created well-defined, plate-like boehmite particles. In this mechanism, the size and shape of the final boehmite particles are not related to the original gibbsite particles.

  - Dehydration of gibbsite and in situ nucleation of boehmite on gibbsite. If the reaction was carried out in an unsealed container, the formation of boehmite followed a different pathway. Gibbsite particles were dehydrated from the (001) planes. Randomly oriented boehmite nucleated on the external and the newly created (001) surfaces. Finally, coagulation of boehmite particles produced fibrous boehmite particles. In this mechanism, the final particle sizes are constrained by sizes of the original gibbsite particles.

- When an organic aluminum precursor, aluminum alkoxide, was used, bayerite was formed initially. However, bayerite was eventually transformed to boehmite.

- The transformation to boehmite was rapid. Normally, an initial incubation time was observed during which period no boehmite was formed. When the boehmite began to nucleate, the transformation usually was completed within one hour.

- The existence of high concentration of single and multi-salts, such as $NaNO_3$, $Fe(NO_3)_3$, etc., gave rise to a longer incubation time but did not change the general behavior for the transformation into boehmite.

Implications

These results suggest that most aluminum-containing phases in tank wastes will be boehmite. This clearly underlines the importance of boehmite particles in the dissolution behavior of the tank waste as well as the colloidal properties of the sludge. Most likely, both mechanisms contributed to the formation of boehmite in tank wastes. The direct transformation of gibbsite to boehmite in the unsealed container may mimic the tank waste condition. However, the tank wastes have aged for many years, giving more crystalline particles with similar particle sizes. Direct dissolution and precipitation were also possible, which would give large crystalline boehmite particles. To predict the efficiency of the tank waste processing (washing and leaching) and the flow properties, the behavior of the dominant boehmite phases must be understood.

Planned Activities

PNNL will collaborate with Savannah River Technology Center and with Albert Hu (CH2M Hill Inc.) to study the solubility boundaries and the associated chemical phases and specifications. The results obtained will be used directly in a semi-empirical approach to calculate the critical flow velocity needed to transfer the tank waste across the pipelines.

Publication

Liu J GJ Lumetta, JW Virden, GL Graff, and NG Colton. 1999. “Characterization of colloidal phases in tank wastes.” *Proceedings of American Ceramic Society*.

Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes

(Project Number: 65368)

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Research Objective

Chromium, one of the problematic elements in tank sludges, is presently considered to be the most important constituent in defining the total volume of high-level waste (HLW) glass to be produced from the Hanford tank wastes. This is because 1) it greatly complicates the vitrification process by forming separate phases in the molten glass and 2) more importantly, sludge washing processes are not effective in removing chromium. Inadequate removal of chromium from sludges could result in production of an unacceptably large volume of HLW glass.

The removal of Cr from tank sludges is complicated by factors that include the complex chemistry of Cr, lack of fundamental data applicable to the HLW chemical systems (high heterogeneity, high ionic strength, high alkalinity, the presence of inorganic and organic ligands, etc.), and the need to avoid processes that may adversely enhance the solubility of plutonium and other actinides. Significant gaps exist in the fundamental understanding of Cr chemistry in tank-like environments. Without such data/understanding, these strategies cannot be appropriately evaluated or optimized. The primary objective of the research being carried out under this project is to develop such data/understanding for HLW tank processing. Pacific Northwest and Lawrence Berkeley National Laboratories, in collaboration with Washington State University, are developing fundamental data on the precipitation/dissolution reactions of Cr(III) compounds and the kinetics of oxidation of Cr(III) to Cr(VI) at room and elevated temperatures and under conditions relevant to high-level waste processing. This integrated approach involving measurement of solubility and oxidation rate constants and spectroscopic characterization of aqueous and solid species as a function of ionic strength, alkalinity, redox conditions, and temperature will provide thermodynamic and kinetic data. These data are necessary to predict changes in Cr solubility and speciation in response to changes in pretreatment strategies or to develop cost-effective tank waste processing technologies that result from reducing the total amount of Cr in processed waste.

Research Progress and Implications

This report summarizes research after 1.5 years of a three-year project. There are two ways of removing chromium from the wastes, solubilization of Cr (III) compounds and the oxidation of Cr(III) to Cr(VI). Progress was made on both of these aspects. Studies were conducted to measure the solubility of $Cr(OH)_3$(am) in NaOH and in mixed solutions containing NaOH and $NaNO_3$ and to determine oxidation of Cr(III) to Cr(VI) by H_2O_2 in alkaline solutions.

The $Cr(OH)_3$(am) was prepared and suspended in NaOH ranging in concentration from 0.01 to 10 M. The observed Cr concentrations in solutions filtered through 0.2 µm and 0.0018 µm were similar, indicating that colloids of sizes >0.0018 µm do not exist in these suspensions and that either of these filters can be used to effectively separate solids from solutions. X-ray diffraction analyses of the solid phases indicated that the solids were amorphous. Oxidation state analyses of most of the aqueous samples by chromatographic technique and of limited samples by x-ray absorption spectroscopy (XAS), carried out at Lawrence Berkeley Laboratory, showed that Cr(III) is the dominant oxidation state in the aqueous and solid phases. The solubility of $Cr(OH)_3(am)$ was observed to increase dramatically with the increase in NaOH concentrations, especially between 1.0 and 10 M where the observed Cr concentrations increased from $10^{-4.5}$ to 0.1 M. A gradual decrease in Cr concentrations was observed at longer equilibration periods, reflecting more likely a change in chemical potential of the solid phase.

The solubility of $Cr(OH)_3(am)$ was also determined in 3.0 M NaOH and in the presence of $NaNO_3$, a major component in tank wastes, ranging in concentrations from 0.1 to 6.0 M. About an order of magnitude increase in chromium concentrations was observed with the increase in $NaNO_3$ concentrations from 0.1 to 6.0 M. As observed with solubility in NaOH, gradual decreases in solubility were observed with the increase in equilibration period. Thermodynamic interpretations of these data will be made using Pitzer formulism to develop models applicable to tank wastes containing concentrated electrolytes.

Chromium (III) in alkaline solutions was found to exist in species with various degrees of oligomerization. A cation exchange technique was used successfully to separate monomeric, dimeric, and trimeric Cr(III) species from the bulk Cr(III) solution. The separated species have been characterized by ultraviolet-visible (UV/Vis) absorption spectroscopy. Kinetic experiments indicate that the three Cr(III) species with lower degrees of oligomerization (monomer, dimer, and trimer) are more easily oxidized by hydrogen peroxide in alkaline solutions than the bulk Cr(III). The oxidation of the monomer, dimer, and trimer followed a first-order reaction with respect to the concentration of Cr and hydrogen peroxide, but a reversed first order with respect to the concentration of NaOH.

Planned Activities

Studies on the solubility of $Cr(OH)_3(am)$ in different electrolytes will be continued. The results will be used to develop a thermodynamic model to predict Cr(III) behavior in tank solutions. We will continue studies of the kinetics of oxidation of Cr(III) to Cr(VI) in the presence of different oxidants and at room and elevated temperatures. The information gained will provide fundamental data for effective oxidants, relevant to tank solutions.

New Silicotitanate Waste Forms: Development and Characterization

(Project Number: 60345)

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Research Objective

The objective of this program is to identify new waste forms and disposal strategies specific to crystalline silicotitanate (CST) secondary waste that is generated from cesium and strontium ion exchange processes. Waste forms that are developed in this work will offer an alternative to current disposal plans. The goals of the program are to reduce the costs associated with CST waste disposal, minimize the risk of contamination to the environment during CST processing, and provide DOE with technical alternatives for CST disposal. The technical objectives of the proposed work are to 1) fully characterize the phase relationships, structures, and thermodynamic and kinetic stabilities of crystalline silicotitanate waste forms and 2) establish a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry.

Research Progress and Implications

This report summarizes work after two years and three months of a three-year project. To date, studies have been performed to 1) determine the durability of waste forms synthesized by heat-treating the UOP CST IE-911, 2) investigate the stable and metastable phase formation, especially the cesium-containing phases from heat-treated CST and from model three-component systems, and 3) investigate thermodynamic stabilities of compounds related to the ion-exchanged CST and the thermally converted oxides.

Durability of Thermally Converted CST

The durabilities of several Cs-loaded, thermally converted CST waste forms have been measured. The Cs-exchanged materials were heat-treated to temperatures ranging from 500° to 1000°C, analyzed by x-ray diffraction (XRD) for phase selection, then characterized for chemical durability. Chemical durability was measured using the standard product consistency test (PCT) and the MCC-1 leach test. The leach rates were extremely low, ranging from 10^{-8} to 0.002 $g/m^2 \cdot day$. The untreated 500° and 900°C materials exhibited the lowest Cs leach rates, and the total fraction of Cs released for these samples was less than 1 wt% after seven days. These thermally converted waste forms are several orders of magnitude more durable than borosilicate glass. The aqueous durability behavior, as measured by the PCT test, for both as-received and Na-exchanged IE-911 loaded to 5 wt% and 12-wt% Cs did not show any significant differences. Leach rates measured using the MCC-1 test were even lower than those measured by the PCT test, as expected.

The durability tests show that heat-treated IE-911 with no additives can result in a chemically durable waste form. Thermogravimetric and differential thermal analysis of Cs-exchanged and Na, Cs-exchanged IE-911 was performed to determine decomposition and crystallization temperatures. This analysis revealed that all molecular water is desorbed by 400°C, and hydroxyl groups are removed near 800°C. Therefore, the risk of radiolytic hydrogen production during short- or long-term storage is eliminated by heat-treating the ion exchanger to temperatures above 800°C. The volume reduction of a pellet heat-treated to 900°C is 40%.

Structure/Property Relationship Studies

Phase Selection of Thermally Converted CST

Phase stability and crystal chemistry studies for compositions related to the exchanger are vital to predicting long- and short-term performance of waste forms. Cs-loaded IE-911 contains six or more constituents, including Cs_2O, Na_2O, SiO_2, TiO_2, binder, and proprietary components. While the phase relationships between some of the binary and ternary components of the CST are available in the literature, the phase selection and durabilities of more complex compositions that represent the loaded exchanger are unknown.

X-ray diffraction of heat-treated IE-911 powders shows that the single-phase metastable ion exchanger structure is destroyed above 500°C, and then at higher temperatures stable multiphase crystalline mixtures precipitate. Positive identification by XRD had already been achieved for the sodium titanate phase, $Na_2Ti_6O_{13}$. To determine whether small amounts of cesium could reside in the $Na_2\ Ti_6O_{13}$ structure, a solid substitution series of $(Na, Cs)_2\ Ti_6O_{13}$ was synthesized, and the lattice parameters were measured by XRD. This study surprisingly revealed that there is no measurable substitution of cesium for sodium on the $Na_2\ Ti_6O_{13}$ lattice, eliminating the possibility that small amounts of cesium could reside in this phase in heat-treated IE-911.

^{133}Cs magic angle spinning (MAS) nuclear magnetic resonance (NMR) measurements were performed to reveal the local environment around the Cs atom. The NMR spectra for NaOH-treated, Cs-exchanged IE-911 heat-treated over a range of temperatures indicate that the Cs environment in the as-received exchanger is destroyed above 500°C. Broadening in the NMR spectrum at 500°C indicates that the material is becoming amorphous. At 700°C a new Cs-containing phase forms, and by 800°C the original Cs environment is completely gone and the Cs is in only one crystalline environment.

A transmission electron microscopy (TEM) study was performed to evaluate the phase selection of thermally converted CST. Among these were Cs, X1, Si oxide, Na, Ti oxide, Na, Ti, X2 oxide, and very minor Na, Cs, Ti, Si, X1 oxide, where X1 and X2 are proprietary components of the ion exchanger. TEM revealed that the majority of the cesium is contained in a Cs, X1, Si oxide. This phase was successfully synthesized using solid-state reaction, sol gel, and hydrothermal reactions. The stoichiometry of the phase is $Cs_2X1Si_3O_9$. Rietveld refinement of x-ray powder diffraction data showed that $Cs_2X1Si_3O_9$ has a hexagonal structure (space group P63/m) with lattice parameters a=7.2303(2) Å, c=10.2682(4) Å. The simulated crystal structure based on the atomic positions of the isomorph and the lattice parameters of $Cs_2X1Si_3O_9$ is shown in Figure 1. It consists of silica tetrahedra and X1 octahedra that form three- and six-membered rings. The largest free aperture of the rings is approximately 2.2x2.6 Å, which is smaller than a cesium atom (~3.5 Å). Therefore, the cesium in this phase will be immobile. Removal of cesium from the structure will require the cleavage of the strong, covalent Si-O and X1-O bonds. This structural feature in part explains the high resistance to leaching of cesium in thermally converted IE-911 that is exposed to aqueous solutions.

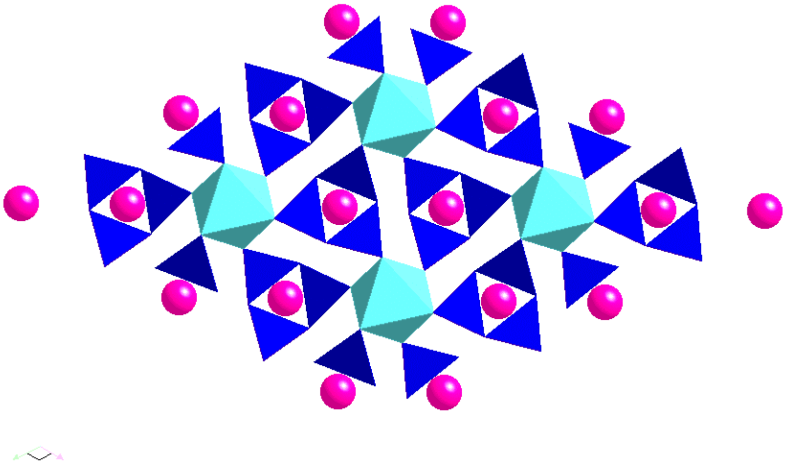

Figure 1. View of $Cs_2X1Si_3O_9$ Structure Down the [001] Directions. This is the major cesium-containing phase in thermally converted (900°C) IE-911.

Radiation stability studies (by gamma irradiation in the PNNL ^{60}Co source as well as by in situ TEM electron beam with the collaboration of Prof. Rod Ewing in University of Michigan) are in progress. Preliminary results from in-situ TEM electron irradiation show amorphization after an electron fluence of $1.1x10^{22}$ e/cm^2.

A second new phase discovered in TEM (Na, Ti, X2, oxide) has a structure similar to $NaX2O_3$. To determine the extent of titanium substitution in the mixed phase, a series of compounds with up to 20% titanium substituted for X2 were synthesized using a sol gel technique. A systematic shift of the lattice parameter as a function of titanium substitution could clearly be observed. Comparison of the heat-treated IE-911 with the synthesized compounds revealed that the phase in IE-911 has 15% titanium substitution on the lattice. The structure of the new compound is related to a perovskite; however, the distribution of the cations in the structure is unknown.

Stable Phases in Cs_2O-TiO_2-SiO_2 System

Phase equilibria studies in the model system, Cs_2O-TiO_2-SiO_2, are being performed to identify the stable compounds and determine their compositional regions of stability. The phase relationships for compositions related to the ion exchanger will provide information necessary for setting optimal composition and temperature regimes for processing the final waste form and will elucidate the effects of minor compositional variations.

Two new high-temperature, durable, high-Ti crystalline zeolitic phases, $CsTiSi_2O_{6.5}$ and $Cs_2TiSi_6O_{15}$, were synthesized and characterized. $CsTiSi_2O_{6.5}$ has a crystal structure isomorphous to the mineral pollucite, $CsAlSi_2O_6$, with Ti^+ replacing Al^+. The structure of

$Cs_2TiSi_6O_{15}$ is unique; titanium octahedra and silicon tetrahedra forming an open framework structure with the Cs residing in large cavities. The largest covalently bonded ring opening to the Cs cavities in both compounds is smaller than a Cs ion, revealing that Cs ion has minimal mobility in the structure. Therefore, both compounds have exceptional resistance to leaching. Single crystal growth experiments have produced a new tetragonal structure that is similar to cubic pollucite (1:2:4 Cs_2O-TiO_2-SiO_2) but with extended TiO_2 solubility. In addition, a new compound with stoichiometry 1:1.2:1.7 Cs_2O-TiO_2-SiO_2 has been identified. Crystal structure determination of these new compounds is in progress.

A complete solid solution substitution series of $CsTiSi_2O_{6.5}$ and $CsAlSi_2O_6$, has been synthesized. These are interesting because the substitution of aluminum by titanium is charge-balanced by the incorporation of additional oxygen ions, converting four-coordinated aluminum to five-coordinated titanium. Thus the rather unusual ionic substitution $Al^{3+} = Ti^{4+} + ½ O^{2-}$ is occurring. Lattice parameters and titanium contents vary in a complex way, especially for Ti-rich compositions. Subambient cubic-to-tetragonal phase transitions in Ti/Al pollucite were studied by x-ray powder diffraction. Under ambient conditions, $CsAlSi_2O_6$ is cubic (space group Ia3d); at subambient temperatures, the structure is tetragonal (space group I4/acd). Substitution of Ti for Al in pollucite ($CsAl_{1-x}Ti_xSiO_{6+y}$) resulted in stabilization of the cubic structure at low temperature (to 100K).

Metastable Phases in Cs_2O-TiO_2-SiO_2 System

Researchers at Sandia National Laboratories (SNL) are studying the metastable phase development in the component systems that represent the cesium-loaded ion exchanger. This work complements the stable phase development studies at PNNL and allows for a complete understanding of the phase development from the metastable ion exchanger to the stable ceramic waste form. Hydrothermal Cs_2O-TiO_2-SiO_2 ternary phase searches have produced two novel phases, which we have designated SNL-A and SNL-B. The stability regions of these phases as a function of Cs_2O:TiO_2:SiO_2 precursor ratio (and pH) are plotted on the ternary diagram in Figure 2. These experiments show a distinct relationship between SNL-B and SNL-A. At 170°C, SNL-B is formed in a mixture with SNL-A. With increased time at temperature, only SNL-A is formed. For example, at 120°C for 5–20 days, only SNL-B is formed, while at 120°C for 28 days, only SNL-A is formed. Also shown on the ternary plot is the stability region for TiO_2 and pharmacosiderite (a known microporous Cs_2O-TiO_2-SiO_2 ion exchanger).

SNL-A is a condensed phase with a formula $Cs_2TiSi_6O_{15}$, polymorphic to the phase synthesized at PNNL by solid-state techniques. The structure of SNL-A has been solved by structure modeling (using density functional theory calculations) and Rietveld refinement. SNL-A crystallizes in the monoclinic (Cc) space group with unit cell parameters:

a = 12.998 (2) Å
b = 7.5014 (3) Å
c = 15.156 (3) Å
β = 105.80 (3)°.

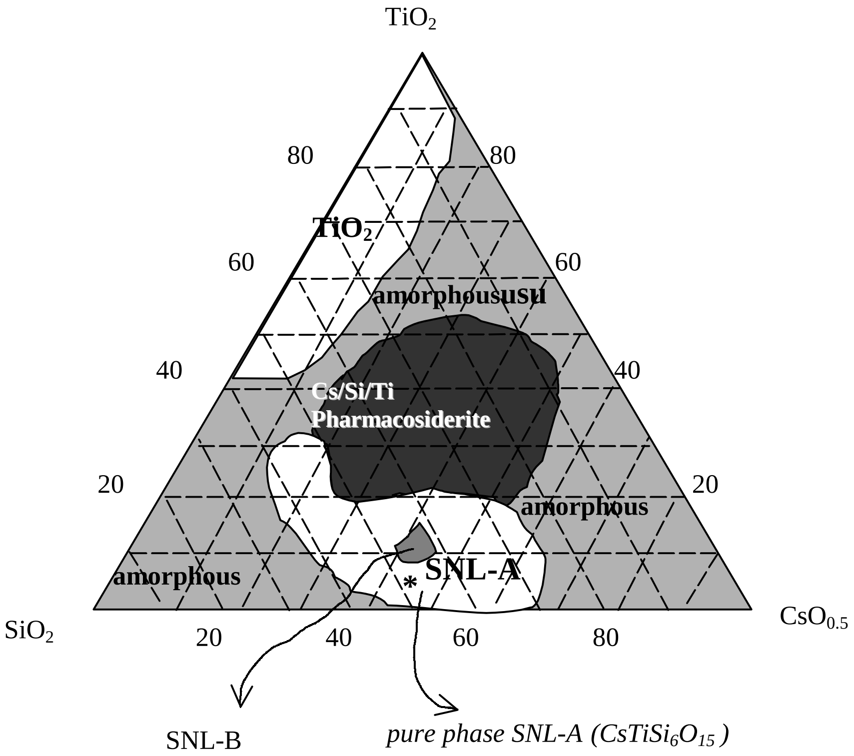

Figure 2. Stability of Hydrothermally Synthesized Cs_2O-TiO_2-SiO_2 Ternary Phases at 170°C

The framework of SNL-A consists of silicon tetrahedra and titanium octahedra, which condense in 3-, 5-, 6-, 7- and 8-rings. The Cs ions are located cages created by the rings. PCT leach tests performed on this phase for 10 days showed <0.2% Cs loss from the original 30% by weight Cs composition; effectively no Cs was lost due to leaching. SNL-B is a microporous ion exchanger with a chemical formula $Cs_3TiSi_3O_{9.5}3H_2O$. This molecular sieve exhibits high selectivity for divalent cations. Solid-state ^{133}Cs and ^{29}Si MAS NMR and cross polarization (CP) MAS NMR of SNL-A and SNL-B reveal that both phases are structurally complex with multiple silicon and cesium coordination sites. All silicon atoms in both phases are in tetrahedral coordination. The CP-MAS NMR experiments show there is internal water in SNL-B and none in SNL-A. This is confirmed by thermogravimetry experiments.

In situ TEM-monitored electron irradiation studies of SNL-A and SNL-B were also carried out, in collaboration with Dr. Rod Ewing at the University of Michigan, to determine the stability of these new phases in radioactive environments. The irradiation-induced transformation of microporous crystalline SNL-B to amorphous material is observed by fading Bragg-diffraction spots in the electron diffraction pattern. The irradiation dose needed for amorphization of SNL-B is inversely dependent on temperature. This corresponds to heat-accelerated cesium and/or water loss, and finally a thermally induced phase change at 500°C (which is also observed by differential thermal analysis). This amorphization behavior is typical of other zeolite materials studied by Dr. Ewing. The condensed phase SNL-A, on the other hand, is very irradiation-resistant. It does not undergo any irradiation damage with very high dose rates.

New Sr-Selective Microporous Ion Exchanger

In the course of Na_2O-TiO_2 hydrothermal phase searches, researchers at SNL discovered a new inorganic molecular sieve, Na/Nb/M/O (M=Ti and Zr), with extreme selectivity for divalent elements, especially Sr and RCRA[a] metals, (Phase I is a Ti-niobate phase, Phase II is a Zr-niobate phase). They are chemically and mechanically stable, have high selectivity for divalent radwaste cations and RCRA metals, are regenerable (by back ion exchange) and thermally converted to a refractory and unreactive perovskite-based ceramic.

Thermodynamic Studies Using Solution Drop Calorimetry

Using hydrothermal methods, two series of microporous silicotitanates were synthesized at SNL: $(Na_{1-x}Cs_x)_3Ti_4Si_3O_{13}(OH)\cdot xH_2O$ (x = 4-5) phases with a cubic structure of $P\bar{4}3m$ (analogs of the mineral pharmacosiderite) and $(Na_xCs_{1-x})_3Ti_4Si_2O_{13}(OH)\cdot xH_2O$ (x = 4-5) phases with a tetragonal structure of $P4_2/mcm$. The enthalpies of drop solution in molten $2PbO\cdot B_2O_3$ at 974K were measured at UC-Davis by high-temperature reaction calorimetry, and the enthalpies of formation have been determined from constituent oxides using appropriate thermochemical cycles. The enthalpies of formation for the cubic phases become more exothermic as Cs/(Na+Cs) increases, whereas those for the tetragonal phases become less exothermic. This result indicates that the cesium uptake in the cubic phases is thermodynamically favorable, whereas that in the tetragonal phases is thermodynamically unfavorable and kinetically driven. In addition, the cubic phases appear to be more stable than the corresponding tetragonal phases with the same Cs/Na ratio. We attribute these disparities in the energetic behavior of the two series to their differences in both local bonding configuration and degree of hydration.

Energetics of Ti-Substituted Pollucites

As stated earlier, a complete solid solution series was synthesized between $CsAlSi_2O_6$ and $CsTiSi_2O_{6.5}$ using sol-gel method at PNNL. The structures of the solid solutions are analogous to that of cubic pollucite ($CsAlSi_2O_6$), as determined by Rietveld analysis of powder synchrotron XRD data. The standard molar enthalpies of formation from the oxides for Ti-substituted pollucites were determined at UC-Davis by drop-solution calorimetry. As Ti^{4+} substitutes for Al^{3+} in pollucites, the enthalpies of formation become less exothermic, suggesting a destabilizing effect of the charge-coupled substitution, $Ti^{4+} + 1/2O^{2-} \rightarrow Al^{3+}$, on the pollucite structure. Moreover, the enthalpic variation shows an exothermic mixing within the composition range

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(a) RCRA=Resource Conservation and Recovery Act.

from $CsTi_{0.3}Al_{0.7}Si_2O_{6.15}$ to $CsTiSi_2O_{6.5}$. This nonideal mixing behavior is consistent with the trend seen in variation of lattice parameters, and we interpret it to be a result of the short-range order associated with the framework cations Al^{3+}, Si^{4+}, and Ti^{4+} in the structures.

Summary

In summary, we have shown that a very durable waste form can be achieved by a simple heat treatment of the Cs-loaded ion exchanger with no additives. Direct thermal conversion reduces the total volume of waste generated from the ion exchanger by 40% and dramatically simplifies processing. Heat treatment of the ion exchanger coarsens fines, reducing inhalation risk, and removes water, eliminating radiolytic hydrogen production. The IE-911 CST ion exchanger is compositionally complex. Transmission electron microscopy, XRD, and synthesis studies have revealed that the major phases in CST are $Na_2Ti_6O_{13}$, $Cs_2X1Si_3O_9$, and $Na(Ti,X2)O_3$. The network structure of the cesium-containing phases precludes facile migration of the cesium ion, resulting in extremely high aqueous durability. Metastable phase-development studies have revealed two new low temperature Cs/Si/Ti phases and a novel class of niobate-based molecular sieves (Na/Nb/M/O, M = transition metals), which show exceptionally high selectivity for divalent cations. These niobate materials have shown orders of magnitude better selectivity for Sr^{2+} under acid conditions than any other material. In addition, the thermodynamic stabilities of metastable and stable compounds have been determined by solution drop calorimetry. This combined information on phase selection as a function of composition, chemical durability, and thermodynamic stability can be used to determine processing windows and to predict long- and short-term stability of thermally converted CST ion exchangers.

Information Access

Balmer ML, Y Su, IE Grey, A Santoro, RS Roth, Q Huang, N Hess, and BC Bunker. 1996. “The structure and properties of two new silicotitanate zeolites.” *In Scientific Basis for Nuclear Waste Management XX*, W. J. Gray and I. R. Triay, eds. Vol. 465, p. 449.

Balmer ML, Q Huang, A Santoro, and R Roth. 1997a. “Neutron powder diffraction study of the crystal structure of $CsTiSi_2O_{6.5}$.” *J. Sol. State Chem*. 130:97-102.

Balmer ML, BC Bunker, LQ Wang, CH F Peden, and Y Su. 1997b. “Solid State ^{29}Si MAS NMR of Titanosilicates.” *J. Phys. Chem*. 101(45):9170-9179.

Balmer ML, Y Su, H Xu, E Bitten, D McCready, and A Navrotsky. 1999. “Synthesis, structure determination, and aqueous durability of $Cs_2ZrSi_3O_9$.” *J. Amer. Ceram. Soc*. (submitted).

Grey IE, RS Roth, and ML Balmer. 1997. “The crystal structure of $Cs_2TiSi_6O_{15}$.” *J. of Sol. State Chem*. 131:38-42.

McCready DE, ML Balmer, and KD Keefer. March 1997. "Experimental and calculated x-ray powder diffraction data for cesium titanium silicate, $Cs_2Ti_2Si_4O_{13}$: A New Zeolite." *Powder Diffraction* 12(1):40-46.

Nenoff TM, JE Miller, SG Thoma, and DE Trudell. 1996. " Highly selective inorganic crystalline ion exchange material for Sr^{2+} in acidic solutions." *Environ. Sci. Technol.* 30:3630.

Nenoff TM, M Nyman, A Navrotsky, H Xu, Y Su, and ML Balmer. 1999. "Synthesis, characterization and ion exchange of novel sodium niobate phases." *In Proceedings from ACS Symposium on First Accomplishments of Environmental Management Science Program,* New Orleans.

Nogues JL, EY Vernaz, and N Jacquet-Francillon. 1984. In *The Scientific Basis for Nuclear Waste Management*, Vol. 44. CM Jantzen, JA Stone, and RC Ewing, eds. Materials Research Society.

Nyman MD, TM Nenoff, Y Su, ML Balmer, A Navrotsky, and H Xu. 1998. "CSTs: Stability and use as alternative waste forms." *In Scientific Basis for Nuclear Waste Management XXII,* DJ Wronkiewicz and JH Lee, eds. Vol. 556, pp. 71-76.

Nyman M and TM Nenoff. 1999. "Synthesis, characterization and ion exchange of new Na/Nb/M4+/OH2O (M = Ti, Zr) phases." *In Proceedings from the Metal Separation Technologies Beyond 2000*, Hawaii.

Nyman M, BX Gu, LM Wang, RC Ewing, and TM Nenoff. 2000. "Synthesis and characterization of a new microporous cesium silicotitanate (SNL-B) molecular sieve." *J. of Microporous and Mesoporous Materials* (submitted).

Su Y, ML Balmer, and BC Bunker. 1997. "Evaluation of cesium silicotitanates as an alternative waste form." *In Scientific Basis for Nuclear Waste Management XX,* WJ Gray and UR Triay, eds. Materials Research Society Vol. 465, pp. 457-464.

Su Y, ML Balmer, L Wang, BC Bunker, MD Nyman, T Nenoff, and A Navrotsky. 1998. "Evaluation of thermally converted silicotitanate waste forms." *In Scientific Basis for Nuclear Waste Management* XXII, DJ Wronkiewicz and JH Lee, eds. Vol. 556, pp. 77-84.

Su Y, ML Balmer, and BC Bunker. 2000. "Raman spectroscopic studies of silicotitanates." *J. Phys. Chem*. (submitted).

Xu H, A Navrotsky, ML Balmer, Y Su, E Bitten, TM Nenoff, and MD Nyman. 1999. "Thermochemistry of substituted pollucites along the CsAlSi2O6-CsTiSi2O6.5 join." *EOS (American Geophysical Union 1999 Fall Meeting)*, Vol. 80, No. 46, F1115.

Xu H, A Navrotsky, MD Nyman, and TM Nenoff. 2000. "Thermochemisty of microporous silicotitanate phases in the Na_2O-Cs_2O-SiO_2-TiO_2-H_2O system." *J. Materials Research* 15(3) (in press).

Yanase I, H Kobayashi, Y Shibasaki, and T Mitamura. 1997. "Tetragonal-to-cubic phase transition in pollucite by low-temperature x-ray powder diffraction." *J. Am. Ceram. Soc*. 80**:**2693.

Actinide-Specific Interfacial Chemistry of Monolayer Coated Mesoporous Ceramics

(Project Number: 65370)

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Specific DOE Problem

This research addresses selective separation, isolation, or sequestration of actinide species from complex waste mixtures for stabilization, characterization, quantification, and permanent disposition.

Research Objective

The objective of this program is to design, synthesize, and evaluate high-efficiency, high-capacity sorbent materials capable of selectively sequestering actinides from complex aqueous mixtures. One of the central goals of this project is to understand the fundamental interfacial science required to develop novel mesoporous materials coated with organized monolayers of rationally designed ligands, custom-tailored for binding specific actinide cations. This capability addresses waste management by separation of actinides, a central concern of high-level waste (HLW) and nuclear materials management at several DOE sites.

Research Progress and Implications

This report summarizes work after 1.5 years of a three-year project. Selective isolation of actinides from a complex mixture is anticipated to increase assay accuracy, speed up analysis turnaround time, reduce waste volume (and cost), and enhance decontamination efficiency and safety.

Novel Silane Synthesis

Extending our studies from last year, we continued to prepare and evaluate new interfacial ligand fields for our self-assembled monolayers on mesoporous supports (SAMMS) sorbent materials. An important class of ligands that have been exploited in actinide solution extraction methods are the carbamoylphosphine oxide (CMPO) ligands. We incorporated several variations of the fundamental CMPO structure into our monolayers (e.g., Ac-Phos, Prop-Phos, etc.)(a). We have also incorporated some of Professor Raymond's plutonium-specific ligands into the SAMMS materials, most notably the hydroxypyridinone (HOPO) and catechol ligands developed and synthesized by the Raymond Group.

Supercritical Fluid (SCF) Methods

In Year 1, we developed powerful new synthetic methods for the deposition of self-assembled monolayers within mesoporous ceramics using supercritical carbon dioxide ($SCCO_2$) as the reaction medium. This new methodology tremendously accelerates monolayer deposition, reduces defect density within the monolayer, increases monolayer stability, and eliminates the drying phase of the SAMMS synthesis as well as virtually eliminating the waste stream resulting

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(a) Ac-Phos = 3-(2-diethylphosphatoacetamido) propyltriethoxylsilane. Prop-Phos= 3-(3-diethylphosphatopropionamido) propyltriethoxylsilane.

from the synthesis. We have now successfully demonstrated with supercritical nitrogen (SCN_2), which is also an effective reaction medium for SAMMS synthesis. $SCCO_2$ is not entirely inert and can undergo reaction with certain classes of molecules. SCN_2 doesn't suffer from this limitation and seems to be every bit as good as $SCCO_2$ for this chemistry.

Last year, our SCF deposition studies focused on the deposition of mercaptopropyl-trimethoxysilane (MPS) as our benchmark model system. Now that we have refined and optimized the synthetic protocol, we extended this capability to include the deposition of more complex materials like ethylenediamine (EDA)-silane and the phosphonate esters Ac-Phos and Prop-Phos.

Lanthanide Model Studies

Due to the expense of performing experiments with actinides, preliminary screening studies were performed using lanthanides as actinide mimics. These pre-screening studies confirmed that SAMMS can bind these target species with high affinity (K_d's over 100,000 were measured, and they were commonly over 30,000), and that the binding affinities of these nanostructured hybrid materials are pH dependent (dropping off with increasing acidity). The binding kinetics of SAMMS was probed and found to be quite rapid—in all cases; equilibrium was reached in less than a minute!

Competition experiments were carried out and revealed only a modest effect from added iron (III) in one case (to form a six-membered ring chelate), and none at all with glycinylurea SAMMS (which forms a seven-membered ring chelate). Regeneration of SAMMS was found to be easily accomplished by a simple acid wash, affording greater than 98% of the original activity.

Actinide Studies

Promising candidates of SAMMS had their binding affinities evaluated with Th, U, Np, Pu and Am. It was found that the phosphonate SAMMS had very high affinities for U, Pu and Am. Particularly noteworthy is the high, and surprisingly pH independent, binding affinity of the phosphonate ester SAMMS (both Ac-Phos and Prop-Phos) for Pu. Clearly, these SAMMS are capable of playing a valuable role in the DOE cleanup effort.

Also noteworthy is that Prop-Phos SAMMS demonstrates a high affinity for Pu and virtually none for Am at the lower pHs. This observation suggests a very simple and direct separation of Pu and Am using SAMMS. In most of the experiments performed, more than 98% of the Pu was sequestered in the SAMMS phase, and >99% of the Am was left behind in solution. Separation of Pu from Am at low concentrations is a critical need in determining the final disposition of HLW, and Prop-Phos SAMMS provides a simple, powerful, and unprecedented capability for achieving this separation. The kinetics of Pu sorption was found to only take a few minutes, and in fact is faster than typical actinide sorbents in use today.

Pertechnetate Separation

We have also developed SAMMS to sequester tetrahedral oxoanions. Thus, we have constructed a version of SAMMS in which the pores are lined with cationic copper (II) ethylenediamine complexes, which serve as anion exchange sites that are selective for certain tetrahedral oxoanions. Cu-EDA-SAMMS was found to be moderately effective at removing pertechnetate from contaminated Hanford groundwater. Drs. Kemner and Kelley (ANL) provided detailed characterization of Cu-EDA-SAMMS adducts, providing key insights into the binding between the copper center and the oxometallate anion.

Planned Activities

In the last year of the project, we intend to extend our actinide studies to include all of the actinides from Th through Am; evaluate the HOPO ligands in a SAMMS matrix; look at actinide competition studies, kinetics, waste simulants and ultimately possibly even actual waste samples (from tank farms, PFP or other Hanford facilities); and perform EXAFS characterization of the pertechnetate/SAMMS adduct.

Information Access

Web pages

http://www.pnl.gov/etd/product/samms/index.htm

http://www.acs.org/government/success/index.html

Publications

Feng X, L Rao, TR Mohs, J Xu, Y Xia, GE Fryxell, J Liu, and KN Raymond. 1999. “Self-assembled monolayers on mesoporous silica, a super sponge for actinides.” *Ceramic Transactions* Vol. 93*, Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries* (IV), pp. 35-42, JC Marra and GT Chandler, eds.

Fryxell GE, J Liu, and S Mattigod. 1999. “Environmental applications of self-assembled monolayers on mesoporous supports (SAMMS).” *Materials Technology* 14:188-191.

Fryxell GE, J Liu, M Gong, TA Hauser, Z Nie, RT Hallen, M Qian, and KF Ferris. 1999. “Design and synthesis of selective mesoporous anion traps.” *Chemistry of Materials* 11:2148-2154.

Fryxell GE and J Liu. 2000. “Designing surface chemistry in mesoporous silica.” *Adsorption at Silica Surfaces*, E Papirer, ed. Marcel Dekker, pp. 665-688.

Fryxell GE, J Liu, SV Mattigod, LQ Wang, M Gong, TA Hauser, Y Lin, KF Ferris, and X Feng. 2000. "Environmental applications of interfacially modified mesoporous ceramics." *Ceramics Transactions*, Volume 94, *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries* (in press).

Kemner KM, X Feng, J Liu, GE Fryxell, L-Q Wang, AY Kim, M Gong, and S Mattigod. 1999. "Investigation of the local chemical interactions between Hg and self-assembled monolayers on mesoporous supports." *J. Synchotron Rad*. 6:633-635.

Liu J, GE Fryxell, M Qian, L-Q Wang, and Y Wang. 2000. "Interfacial chemistry in self-assembled nanoscale materials with structural ordering." Invited contribution to *Pure and Applied Chemistry* 72:269-279.

Liu J, GE Fryxell, S Mattigod, TS Zemanian, Y Shin, and L-Q Wang. 2000. "Synthesis and applications of functionalized nanoporous materials for specific adsorption." *Studies in Surface Science and Catalysis*, A Sayari et al., eds. Elsevier, Vol. 129, pp. 729-738.

Mattigod S, GE Fryxell, X Feng, and J Liu. 1999. "Self-assembled monolayers on mesoporous supports for metal separation." *Metal Separation Technologies Beyond 2000: Integrating Novel Chemistry with Processing*, KC Liddell and DJ Chaiko, eds. The Minerals, Metals and Materials Society, pp. 71-79.

Mattigod S, X Feng, GE Fryxell, J Liu, and M Gong. 1999. "Separation of complexed mercury from aqueous wastes using self-assembled mercaptan on mesoporous silica." *Separation Science and Technology* 34:2329-2345.

Awards

Ken M. Kemner received the "Presidential Early Career Award for Scientists and Engineers," awarded by the President of the United States, and the "Office of Science Early Career Scientist Award," awarded by the United States Department of Energy.

Electroactive Materials for Anion Separation: Technetium from Nitrate

(Project Number: 65409)

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Research Objective

Many contaminants of interest to the U.S. Department of Energy (DOE) exist as anions. These include the high-priority pollutants chromate, pertechnetate, and nitrate ions. In addition, there are also industrial and urban applications where the separation of anionic species from aqueous streams is critical. Examples include industrial water recycle and waste water treatment (e.g., chloride ion removal for the pulp and paper industry, borate ion in the chemical and nuclear industries) and drinking water and agricultural waste treatment (e.g., nitrate removal).

In the proposed research, technetium is chosen as the target pollutant. Because of its half-life of 213,000 years, technetium (^{99}Tc) presents a long-term hazard for waste disposal. Much of the ^{99}Tc in the tank wastes is present as pertechnetate (TcO_4^-), accounting for its high solubility and mobility in aqueous systems. Several sorbents are available for removing TcO_4^- from alkaline waste brines, but each has important drawbacks. The use of commercial ion exchange (IX) resins to extract TcO_4^-, e.g., Reillex™-HPQ (Reilly Industries) and ABEC 5000 (Eichrom Industries), generates significant secondary waste. The elution of TcO_4^- from Reillex™-HPQ resins requires either concentrated nitric acid or a concentrated caustic solution of ethylenediamine containing a small amount of tin chloride. This eluant has a short shelf life requiring frequent preparation, and the ^{99}Tc is delivered in a complexed, reduced form. While TcO_4^- can be eluted from ABEC 5000 resins using deionized water, the much smaller capacity of ABEC 5000 resins compared with the Reillex™-HPQ resins leads to a low column capacity. In general, unwanted secondary wastes are generated because 1) the only effective eluant happens to be hazardous and/or 2) the IX material has a low capacity or selectivity for the target ion, resulting in more frequent elution and column replacements.

Alternative IX materials that have high capacities, can be regenerated easily, and are highly selective for TcO_4^- would avoid these problems. Electrochemically active IX media meet these criteria. Such an IX system uses electrically induced changes in the media to expel sorbed ions through a charge imbalance rather than requiring chemical eluants to “strip” them. Therefore, this medium eliminates the need to prepare, store, and dispose of many of the process chemicals normally required for IX operations.

The focus of the project is to develop a fundamental understanding of how the physical and chemical properties of electroactive ion exchange (EaIX) materials control their efficiency when used as mass separation agents. Specifically, the desirable characteristics of EaIX materials for separation applications are 1) high reversibility, 2) high selectivity, 3) acceptable physical and chemical stability, 4) rapid intercalation and de-intercalation rates, and 5) high capacity. Because of these requirements, EaIX materials have many properties in common with conventional ion exchangers and electroactive polymers. For example, EaIX materials require the selectivity typically found in ion exchangers; they also require the redox reversibility of electroactive polymers. The results of this work will allow the rational design of new materials and processes tailored for the separation of specific anions.

Research Progress and Implications

This report summarizes work completed in the first 17 months of a three-year project. The two components of the project are synthesis and characterization of EaIX materials. The monomer constituents of the electroactive polymer ultimately control the desirable characteristics described earlier. We have, therefore, focused our efforts in the synthesis monomers with the appropriate functional groups. Synthesis of materials that are stable under highly alkaline conditions has been one of our priorities. We have recently synthesized new ferrocene-containing polymers that, under alkaline conditions, exhibit more stability than commercially available polyvinylferrocene (PVF). Figure 1 compares the characteristics of PNNL-synthesized and commercially available PVF polymers; the commercial PVF is deactivated in less than two cycles. Although PNNL PVF-11 is mainly deactivated after 20 cycles, our study in which we are systematically modifying the basic ferrocene units to make the resulting polymer more stable in alkaline conditions is not completed, and we are hopeful that we will successfully synthesize alkaline-stable electroactive polymers. We have successfully synthesized vinyl-ether ferrocene monomers; these monomers will allow us to systematically study the effects of charge site mobility and molecular weight on characteristics (mainly stability and intercalation rates). Initial attempts of using phase-inversion techniques with commercial PVF for making high-capacity electrodes have failed; this has been attributed to the inability to make highly concentrated solutions. In addition, variabilities in commercially available PVF have made systematic studies of the process conditions difficult. PNNL is currently synthesizing polymers to overcome both of these difficulties. Studies on the application of phase-inversion techniques for making high-capacity electrodes are continuing using model polyaniline polymers.

The methods for obtaining in situ x-ray absorption spectroscopy (XAS) on PVF electrodes in perrhenate (ReO_4^-) electrolytes have been refined and improved at Brookhaven National Laboratory. Most of the problems in collecting spectra at the Fe-K edge accrue from the large background from the ReO_4^- ions. This has been resolved by reconfiguring the electrodes in the spectroelectrochemical cell. It was necessary to optimize the x-ray optics in two separate x-ray

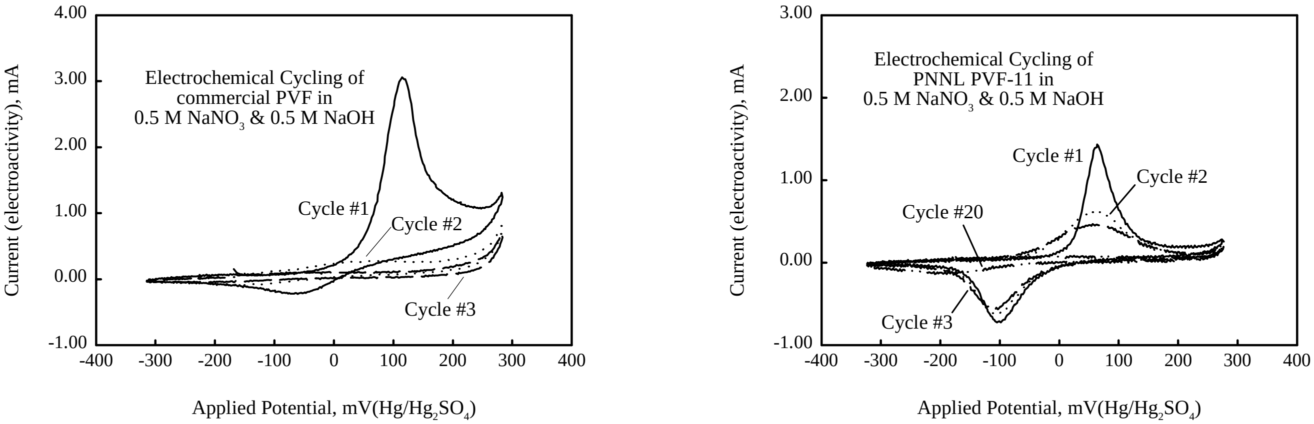

Figure 1. Comparison of PNNL-Synthesized and Commercially Available PVF Polymers

scans to obtain good near edge (XANES) and extended fine structure (EXAFS) spectra. Spectra have also been obtained ex situ at the Fe-K edge on several electrodes prepared from polymer materials synthesized at PNNL. XAS and electrochemical studies were also performed on ferrocenium perrhenate, dimethylferrocenium perrhenate and ferrocenium nitrate, which were synthesized at BNL. The electrochemical studies indicated a stronger interaction of the perrhenate anion with the ferrocenium cation than that seen with the nitrate anion.

Planned Activities

We plan to have alkaline-stable electroactive polymers by June 2000. We plan to prepare polymers ready for further phase-inversion studies by October 2000. The recently obtained XAS results mentioned above are currently being analyzed.

Information Access

Gronda AM and WH Smyrl. October 1999. “High capacity electroactive polymers for radioactive waste removal.” Oral presentation at the 196th Electrochemical Society Meeting, Honolulu.

Hubler TL, GM Anderson, JH Sukamto, MA Lilga, and SD Rassat. August 1999. “Polyvinylferrocene (PVF) polymers as electroactive ion-exchange materials for separation of pertechnetate ion from high nitrate ion containing wastes: Issues and synthetic strategies.” Poster presented at the 218th ACS National Meeting, New Orleans.

Sukamto JH, SD Rassat, RJ Orth, and MA Lilga. 2000. “Electrochemical Ion Exchange.” To appear in the *Encyclopedia of Separation Science*, Academic Press.

Modeling of Spinel Settling in Waste Glass Melter

(Project Number: 65422)

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Problem Addressed

The acceptance criteria for high-level waste (HLW) glass allow a substantially higher waste loading than current melters can handle. The particular processing constraint that limits waste loading is the requirement that the liquidus temperature of HLW glass should be lower than 1050ºC to avoid melter failure due to an excessive settling of spinel.(a) However, this *ad hoc* requirement, which is not based on a rigorous assessment of the safe rate of solid material (mainly spinel) deposition in the melter, is costly. Each 1 mass% decrease in waste loading at Hanford will cost DOE approximately $600,000,000. Fortunately, waste loading could potentially be increased by several percent even with the currently used melters without producing an unacceptable risk to melter performance. The acceptable fraction of spinel in molten glass depends on several factors, such as the size and number density of spinel crystals, the temperature and velocity fields in the melter, and the spinel sludge rheology.

Research Objective

Our objective is to determine the fraction and size of spinel crystals in molten HLW glass that are compatible with low-risk melter operation. To this end, we are investigating spinel behavior in HLW glass and obtaining data to be used in a mathematical model for spinel settling in a HLW glass melter. We will modify the current glass-furnace model to incorporate spinel-concentration distribution and to predict the rate of spinel settling. Also, we will determine the nucleation agents that control the number density and size of spinel crystals in HLW glass.

Research Progress

We have studied the following aspects of spinel behavior in HLW glass:

- spinel formation during the initial melting stages
- the rates of dissolution and crystallization of spinel as a function of temperature
- the equilibrium concentration of spinel as a function of temperature, oxygen partial pressure, and glass composition
- the composition of spinel as a function of temperature
- the effect of temperature history and minor components on the number density and the size of spinel crystals
- the rate and mode of spinel settling

(a) Spinel are compounds having the general structure $M^{II}M^{III}O_4$.

- the rheological properties of spinel sludge in molten glass
- the physical characteristics of the spinel-glass system.

Additionally, we have developed

- a mathematical model describing the electric, temperature, and velocity fields in an HLW melter
- a mathematical model of spinel settling in a limited volume of melt
- a physical model to verify the results of the mathematical models.

These results have been reported in the form of publications in conference proceedings and peer-reviewed journals (see the list below). Some major achievements are described below.

The first spinel crystals form during the initial melting stages, precipitating from the nitrate melt within the bed of reacting melter feed. Spinel formation peaks when the nitrate decomposition is nearly complete and the glass-forming melt is established. These crystals, which do not contain Cr, dissolve in the glass-forming melt during the final stages of conversion. Cr-containing spinel forms when the temperature of molten glass drops below the liquidus temperature.

As the melter model shows, the temperature history of the melt in the HLW glass melter is rather wild. A spinel crystal may undergo several cycles of partial dissolution and growth before reaching its final destination, either in the glass canister or at the melter bottom.

The number density of spinel crystals depends on the presence of minor components, such as RuO_2, Ag_2O, or TiO_2, and may vary from 1 to 10^4 crystals per mm^3. As a result, spinel crystal size may vary from 1 to 100 μm. The size of spinel crystals is the key factor determining the settling rate.

Laboratory studies of spinel formation must simulate melter conditions (in solid glass that has been powdered before heat treatment, spinel crystallization is affected by low-temperature nucleation and surface crystallization).

The rates of crystal growth and dissolution depend on melt temperature and on the crystal number density, which in turn is determined by the presence of heterogeneous nuclei provided by some minor waste components. Above liquidus temperature, when crystals move within the melt by buoyancy, the rate of dissolution of spinel crystals is constant at constant temperature. The size of growing crystals can be approximated by an exponential function of time with the rate coefficient that is an Arrhenius function of temperature.

The concentration of spinel in the melt depends on melt temperature, composition, and oxygen fugacity. These functions were expressed in the form of constitutive equations to be used in mathematical models of HLW glass melters and in models for glass formulation, waste retrieval, blending, and pretreatment.

Planned Activities

- Study the effects of nucleation agents on crystal size and settling rate.

- Develop a theoretical model for dissolution/growth of spinel crystals under nonisothermal conditions.

- Study the dissolution/growth of spinel crystals in periodically increasing and decreasing temperature.
- Compute spinel distribution within the melter and calculate the rate of growth of the spinel sludge bottom layer using the following step-by-step approach:

  - Step 1: Spinel crystals enter the melt from the cold cap. Crystals do not change during the process.
  - Step 2: Spinel is at equilibrium with molten glass.
  - Step 3: Melt redox is a function of temperature. Oxygen bubbles evolve as the temperature of glass increases. Bubbles affect melt density, influencing the temperature and velocity fields.
  - Step 4: Spinel crystals dissolve and grow out of equilibrium in response to temperature and redox.
  - Step 5: Bubble motion and spinel settling produce cellular convection in a melt; spinel may agglomerate.
  - Step 6: Simulate melter conditions for West Valley and Savannah River melters. Compare sludge-thickness calculation with measured values.

Information Access

The following papers have been published or are in the process of publication:

Hrma P. 1999. “Modeling of spinel settling in waste glass melter.” In *Science to Support DOE Site Cleanup*.” PNNL-12208, Pacific Northwest National Laboratory, Richland, Washington.

Hrma P, JD Vienna, JV Crum, GF Piepel, and M Mika. 2000. “Liquidus temperature of high-level waste borosilicate glasses with spinel primary phase.” *Proc. Mat. Res. Soc.*

Izak P, P Hrma, and MJ Schweiger. 2000. “Nonisothermal crystallization of spinel from a high-level waste feed.” *Proceedings of American Chemical Society*.

Izak P, J Klouzek, and P Hrma. 2000. "Evolution of crystalline phases during high-level waste feed-to-glass conversion." To appear in *Ceramic Transactions*.

Izak P, P Hrma, JD Vienna, and B Wilson. 2000. "Effect of Oxygen Partial Pressure on liquidus temperature with spinel primary phase." To appear in *Ceramic Transactions*.

Klouzek J, J Alton, TJ Plaisted, and P Hrma. 2000. "Crucible study of spinel settling in high-level waste glass." To appear in *Ceramic Transactions*.

Klouzek J and A Franek. 2000. "Physical and mathematical modeling of spinel settling in high-level waste glass." *Proceedings of Waste Management 2000*, Tucson, Arizona.

Mika M, JV Crum, and P Hrma. 1999. "Spinel precipitation in high-level waste glass." *Proceedings of the 5th ESG Conference*, Prague, Czech Republic.

Mika M, P Hrma, and MJ Schweiger. 2000. "Rheology of spinel sludge in molten glass." *Ceramics-Silikaty.*

Plaisted TJ, J Alton, P Hrma, and B Wilson. 2000. "Spinel nucleation and growth in high-level waste glass." To appear in *Ceramic Transactions*.

Plaisted TJ, F Mo, B Wilson, and P Hrma. 2000. "Surface crystallization of spinel and acmite in high-level waste glass." To appear in *Ceramic Transactions*.

Schill P and P Vlcek. June 1999. "Mathematical model of radioactive waste glass melter." *Proceedings of the Fifth International Seminar on Mathematical Simulation in Glass Melting,* pp.112–118. Horni Becva, Czech Republic.

Schill P, A Franek, M Trochta, P Viktorin, and P Vlcek. June 1999. "Integrated glass furnace model." *Proceedings of the Fifth International Seminar on Mathematical Simulation in Glass Melting*, pp. 125–137. Horni Becva, Czech Republic.

Stachnik MW, P Hrma, and H Li. 1999. "Effects of high-level waste glass composition on spinel precipitation." *Ceram. Trans*. 107.

Ion Exchange Processes and Mechanisms in Glasses

(Project Number: 60362)

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Research Objective

Plans for immobilizing low-activity radioactive tank wastes at the Hanford Site call for vitrification followed by shallow subsurface disposal. Water percolating through the disposal system will eventually react with the vitrified waste, releasing the encapsulated radionuclides. Consequently, it is important to understand the glass corrosion mechanisms that ultimately control the radionuclide release rate. One important reaction involves the exchange of alkali ions in the glass with H^+ or H_3O^+ ions in water, which raises the pH in the disposal system and can enhance ^{99}Tc release rates by 100X or more. The objective of this work is to develop an understanding of the processes and mechanisms controlling alkali ion exchange and to correlate the kinetics of the ion-exchange reaction with glass structural properties. The fundamental understanding of the ion-exchange process developed under this study is targeted at developing lower ion-exchange rate glasses that would remain durable at higher alkali waste loading.

Research Progress and Implications

Sodium ion exchange and matrix dissolution rates were determined on Na_2O-Al_2O_3-SiO_2 (Series I), Na_2O-Al_2O_3-B_2O_3-SiO_2 (Series II), and several complex boroaluminosilicate glass compositions (Series III). The Series I glass compositions vary in Al_2O_3 content while keeping the ratio of $^{[Q3]}$Si to total Si approximately constant. This was done to monitor the effect of decreasing concentration of nonbridging oxygen (NBO) sites as the available Na^+ is used to form network repolymerizing AlO_2Na ($^{[4]}$Al) tetrahedral sites. These glasses were also doped with trace amounts of Mo (~0.1 mass% MoO_3), which was used as a tracer of matrix dissolution. In the Series II and III glasses, B was used to index matrix dissolution. The Series II glasses were formulated such that Al_2O_3 was swapped for B_2O_3, keeping the Na_2O and SiO_2 mol% constant. This was done to examine differences in Na ion-exchange rates as BO_2Na ($^{[4]}$B) tetrahedral sites are converted to AlO_2Na ($^{[4]}$Al) tetrahedral sites. The Series III glasses were selected as representative low-activity waste glasses based upon propriety glass formulation information received from British Nuclear Fuels Limited, Inc., although the Series III compositions themselves are not proprietary.

Glass-Water Reaction Experiments

Sodium ion-exchange rates were determined by a series of single-pass, flow-through (SPFT) experiments. Glass matrix dissolution was minimized in these experiments by pre-saturating the influent buffer solution with respect to amorphous silica. Experiments were conducted at 25°C and a constant pH of 8. The Series I glasses showed an increasing sodium ion exchange rate with decreasing Al_2O_3 content in the glass. Sodium release rates were ~100X faster than matrix dissolution, indicating the dominance of the alkali ion exchange reaction in silica-saturated solutions. In silica-saturated D_2O solutions, the Na ion exchange rate was ~30% slower than rates in H_2O. This is convincing evidence that the rate-limiting step in the ion exchange reaction involves the transfer of a proton and not other species such as H_3O^+ or H_2O. Ion exchange rates were found to increase with temperature with an activation energy of approximately 50 kJ/mol, which is 40% lower than typical activation energies (≈80 kJ/mol) for silicate glass matrix dissolution. This is consistent with the rate-limiting reaction for ion exchange involving rupture of a weaker O-H bond as compared with dissolution of the silicate matrix, which involves rupture of the stronger Si-O bond. SPFT experiments with Series III compositions also showed the strong influence that glass structure has on reactivity; sodium-exchange rates were found to decrease with an increasing ratio of network formers to network breakers in the glasses.

Glass Reaction Layer Analyses

Reaction layers in Series I glass compositions reacted with isotopically labeled $D_2{}^{18}O$ silica-saturated solutions were analyzed by nuclear reaction analysis (NRA). The magnitude of sodium depletion decreased with increasing Al_2O_3 content in the glasses. Sodium depletion profiles reveal at least three different regions in the reaction layer: 1) surface reaction zone, 2) mixed reaction-diffusion zone, and 3) inter-diffusion zone. Because of surface silanol condensation reactions, peak concentrations of ^{18}O and D occur at different depths. Accordingly, $^{18}O/D$ ratios vary with depth but reach near-constant values (between 1/2 to 1/3) in the inter-diffusion zone near the unreacted glass/gel layer interface. In general, the $^{18}O/D$ ratios are consistent with H_3O^+ as the principal diffusing hydrogen species.

NMR Studies

Magic angle spinning nuclear magnetic resonance (MAS-NMR) was performed on the Series I and Series II glasses at the EMSL User Facility at PNNL. The ^{29}Si chemical shift value became less negative as the Al_2O_3 content increased. This is consistent with the average chemical bond strength of the glass network increasing as Al_2O_3 is added. The ^{27}Al NMR spectra of all the Al_2O_3-containing glasses were nearly identical and were indicative of nearly all (>98%) of the aluminum being tetrahedrally coordinated. The ^{11}B NMR spectra of the Series II glasses were generally resolvable into overlapping narrow- and broad-line width components. The narrow component is due to tetrahedrally coordinated boron, $^{[4]}B$ (i.e., network forming sites). The broad component, on the other hand, is from boron coordinated to three equivalent oxygens to form trigonal planar complexes. Deconvolution of these two peaks and subsequent integration allowed for direct determination of the fraction of four-coordinate boron in the glasses.

XAS Studies

The local Na environment in Series I glass samples were analyzed at the Advanced Light Source (ALS) with x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS) techniques. Both the Na-O bond length and the Na-O peak width decrease with the increase of Al content in the glass. The decrease in Na–O peak width with increasing Al content suggests a decrease in coordination number and increased order around the Na atoms. This is reasonable because the increase of Al_2O_3 content increases the number of tetragonally coordinated Al atoms, which are more negatively charged compared with the Si-O tetrahedron. The more negatively charged AlO_2Na ($^{[4]}Al$) tetrahedra attract Na^+, thereby decreasing the average Na-O bond length and increasing the order (and possibly reducing coordination) around the sodium atoms. In summary, the EXAFS measurements show greater order and tighter bonding of sodium in the glass structure as Al_2O_3 is added. This is consistent with the lower rate of sodium ion exchange observed for these glasses.

Planned Activities

Complete glass-water reaction experiments will be performed with Series II glass. This will include investigating temperature effects on matrix dissolution and Na-release in both H_2O and D_2O. We will relate differences in Na-H exchange to structural changes determined by multiple techniques (NMR, XPS, XAS).

We will complete detailed investigations of Series III glass. We will elucidate the effects of systematic addition of La, Hf, and Zr on glass structure and Na ion exchange rates.

Information Access

Chen Y, BP McGrail, and DW Engel. 1997. "Source-term analysis for Hanford low-activity tank waste using the reaction-transport code AREST-CT." *Mat. Res. Soc. Symp. Proc*. 465:1051-1058.

McGrail BP, JP Icenhower, DK Shuh, JG Darab, DR Baer, S Thevuthasen, V Shutthanandan, and MH Englehard. 2000. "The structure of Na_2O-Al_2O_3-SiO_2 glasses and its impact on sodium ion exchange in H_2O, D_2O, and $D_2{}^{18}O$. *J. Non-Cryst. Solids* (submitted).

Thevuthasan S, V Shutthanandan, DR Baer, EM Adams, S Maheswaran, and MH Engelhard, JP Icenhower, and BP McGrail. 2000. "High energy ion beam studies of ion exchange in a Na_2O-Al_2O_3-SiO_2 glass." *Applied Surface Science* (submitted).

Decontamination and Decommissioning

Microbially Promoted Solubilization of Steel Corrosion Products and Fate of Associated Actinides

(Project Number: 64931)

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Research Objective

The research is designed to evaluate the impact of metal-reducing bacteria on the release of radionuclides, specifically uranium and plutonium, from iron hydroxide minerals formed on the surfaces of corroding mild and stainless steels. The ultimate goal is to develop a safe and effective biological approach for decontaminating mild and stainless steels that were used in the production, transport, and storage of radioactive materials.

Problem Addressed

DOE needs statements call for "biological and physical chemical parameters for effective decontamination of metal surfaces using environmentally benign, aqueous-based biopolymer solutions and microbial processes with potential for decontaminating corroding metal surfaces." Improved understanding of the fundamental processes of microbial reductive dissolution of iron oxide scale on corroding carbon steel will support assessment and potential application of an environmentally benign and cost-effective strategy for in situ decontamination of structural metal surfaces and piping. The research also addresses issues related to the development of oxide-reducing biofilms on steel surfaces under hydrated but nonsaturating conditions.

Research Progress and Implications

This report summarizes accomplishments after one and a half years of a three-year project. Significant advances have been realized in each aspect of the proposed research.

The research is structured into four primary tasks that are being addressed by members of the collaborative team.

- Task 1 investigates the factors controlling the attachment to and release from oxide scale that forms on corroding mild and stainless steel by metal-reducing bacteria.

- Task 2 probes the effects of iron oxide composition and surface properties on cell attachment and biofilm formation.

- Task 3 examines and quantifies the reductive dissolution of synthetic iron oxide thin films as well as the reductive dissolution of iron oxide scale on corroding steel in the presence and absence of soluble electron shuttles that can enhance the rate and extent of enzymatic iron reduction.

- Task 4 determines the distribution of actinides released from iron oxides during reductive dissolution of scales that are colonized by metal-reducing bacteria. Particular attention will be given to the processes that direct the incorporation of actinides into the biomass.

Due to the brief format of this report, results and major implications are summarized to provide a generalized summary of salient points. This research provides information needed to develop optimal approaches for 1) delivering and distributing cells to contaminated corrosion films, 2) determining the fate of contaminants affected by attached bacteria, and 3) recovering contaminants for further processing.

> *Reduction and fate of Pu(IV) by metal-reducing bacteria.* Iron-reducing bacteria were tested for their ability to reduce insoluble Pu(IV), provided as PuO_2, to soluble Pu(III). The fate of Pu(III) was determined using neodymium, Nd(III), as a nonradioactive analogue. The significant results demonstrated that
>
> - Iron-reducing bacteria enzymatically reduced insoluble Pu(IV) to Pu(III).
> - At pH values approaching 6, Pu(III) sorbed to cell surfaces.
> - Cell biomass provides a significant sink for accumulation of actinides

Considering the sorption of Pu(III) with microbial biomass, mechanisms of attachment and detachment to solid substrata (e.g., crystalline and poorly crystalline iron oxides typically associated with corrosion films) were examined in detail.

> *Cell attachment*. Adhesion of the iron reducing bacterium *Shewanella alga* strain BrY to hydrous ferric oxide, goethite, and hematite was examined. The results demonstrated that
>
> - The bacteria readily adhere to both crystalline and amorphous Fe(III) oxide surfaces.
> - Adhesion of *S. alga* strain BrY to hydrous ferric oxide (HFO) correlates with ionic strength, and thus is accurately described by the DLVO theory.
> - The rate of solid phase iron reduction was directly correlated with adhesion of cells with surfaces and hence with the ionic strength of the medium.

Attachment of cells to the crystalline iron oxide hematite was also examined. Genes encoding for green fluorescence protein (GFP) were inserted into iron-reducing bacteria. Thus cells were imaged by confocal laser microscopy as they entered an anaerobic flow chamber and attached to the surfaces of specular hematite. Microscopy studies were carried out at the EMSL facility at PNNL. Figure 1 illustrates the distribution of cells on the hematite surfaces.

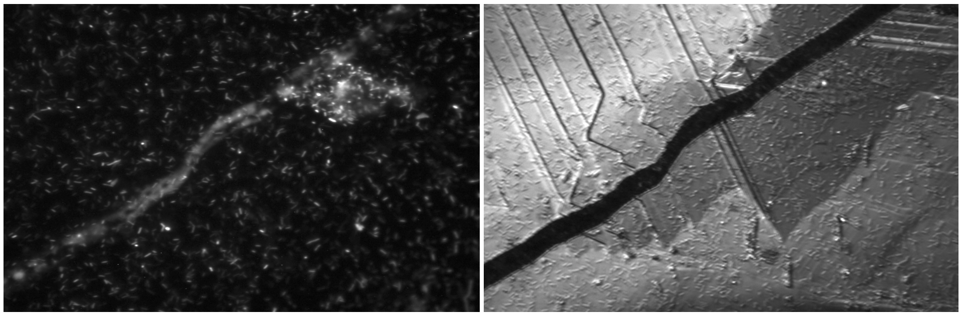

Figure 1. Images Taken on a (001) Hematite Surface of Strain *S. Putrefaciens* Strain MR1 (p519nGFP) After 52 Hours. Bright cells are particularly associated with the step edge. DIC images (left) were captured using and exposure of 32 msec, epifluorescence images (right) with an exposure of 7 sec. Gain for all images was 4 dB.

Results from this work demonstrated that:

- Primary cells adhesion occurred through flagellar attachment.

- Cells were heterogeneously distributed on hematite surfaces, with preferential attachment observed at cracks, steps, and crystal defects.

- Luminescence was greater with cells attached at the cracks, steps, and defects, suggesting that cells were metabolically active at these sites.

Cell detachment. Considering the ability for metal reducing bacteria to reduce and accumulate plutonium, approaches for removing or detaching cells from oxide surfaces were investigated. Cells attached to hematite surfaces were starved for electron donor and other nutrients required for growth. As shown in Figure 2, results demonstrated that

- Cells treated in this manner formed small (100 nm) vesicles on the cells' surface.
- Cells began to detach from the mineral surface
- Vesicles remained attached to the mineral surface.

Recent results show that these vesicles can enzymatically reduce metals and, therefore, have implications for the fate of multivalent radionuclides that are subject to enzymatic reduction.

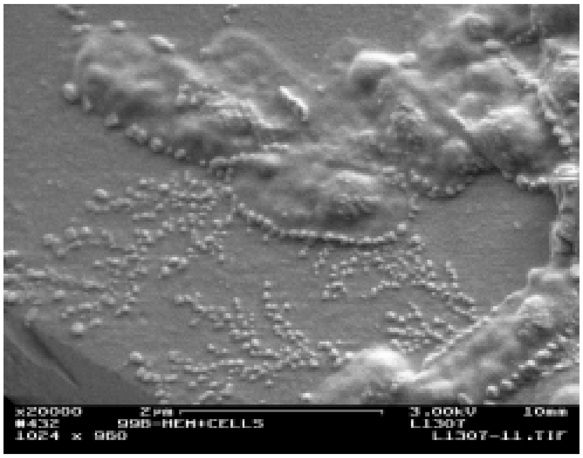

Figure 2. SEM Image of Bacterial Cells with Attendant Vesicles on a Hematite Crystal

Planned Activities

The remainder of the project will focus on

- Describing the role vesicles play in radionuclide reduction and accumulation

- Optimizing conditions for biomass/radionuclide recovery

- Evaluating decontamination of activated corrosion films

- The proposed research is expected to be completed within the timeframe of the project.

Information Access

Das A and F Caccavo. 2000. *Adhesion of the dissimilatory Fe(III)-reducing bacterium Shewanella alga BrY to crystalline Fe(III) oxides* (submitted).

Das A and F Caccavo. 2000. *Dissimilatory Fe(III) Oxide Reduction by Shewanella alga BrY Requires Adhesion* (submitted).

Gorby Y, D Weaver, C Brown, M Romine, and A Neal. 2000. *Expression of Green Fluorescence Protein in Dissimilatory Iron Reducing Bacteria* (submitted).

Contaminant-Organic Complexes, Their Structure and Energetics in Surface Decontamination Processes

(Project Number: 64947)

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Research Objective

There are many compounds that are naturally occurring biodegradable organic chelates (siderophores) and appear to be more effective at oxide dissolution and actinide complexation than ethylenediaminetetraacetic acid (EDTA) or other organic acids currently used in decontamination processes. These chelates bind hard acids [Fe(III) and actinides(IV)] with extraordinarily high affinities. For example, the binding constant for the siderophore enterobactin with iron is about 10^{50}, and its binding constant for Pu(IV) is estimated to be as high. Hence, this project is investigating the efficacy of using siderophores (or siderophore-like chelates) as decontamination agents of metal surfaces. The specific goals of this project are as follows:

- To develop an understanding of the interactions between siderophores (and their functional moieties), Fe and actinide oxides, their surface chemical properties that foster their dissolution and the conditions that maximize that dissolution.

- To develop the computational tools necessary to predict the reactivity of different siderophore functional groups toward oxide dissolution and actinide (IV) solubilization.

- To identify likely candidate chelates for use in decontamination processes.

To meet these objectives, the project combines x-ray absorption spectroscopy (XAS) and computational chemistry to provide basic information on the structure and bonding of siderophore functional groups to metal (Fe and U) oxide specimens common to corrosion products and scales on carbon steel and stainless steel encountered in DOE facilities. The project explores fundamental scientific aspects of oxide mineral surface chemistry and dissolution related to chelate-induced solubilization. The spectroscopic and computational aspects of this project are complemented by macroscopic dissolution and solubilization studies of oxides and associated contaminants. From this combination of molecular, macroscopic, and computational studies, structure-function and structure-reactivity relationships will be developed. These tasks are centered on investigative themes: 1) macroscopic dissolution studies (C. Ainsworth, PNNL), 2) optical spectroscopy (C. Ainsworth [PNNL]), 3) x-ray absorption spectroscopy (XAS) (S. Traina [OSU] and S. Myneni [LBNL]), and 4) computational chemistry (B. Hay [PNNL]).

Research Progress and Implications

This report summarizes research after 1.5 years of a three-year project. Initial investigations have centered on dissolution, computational chemistry, and XAS; XAS results are not reported here.

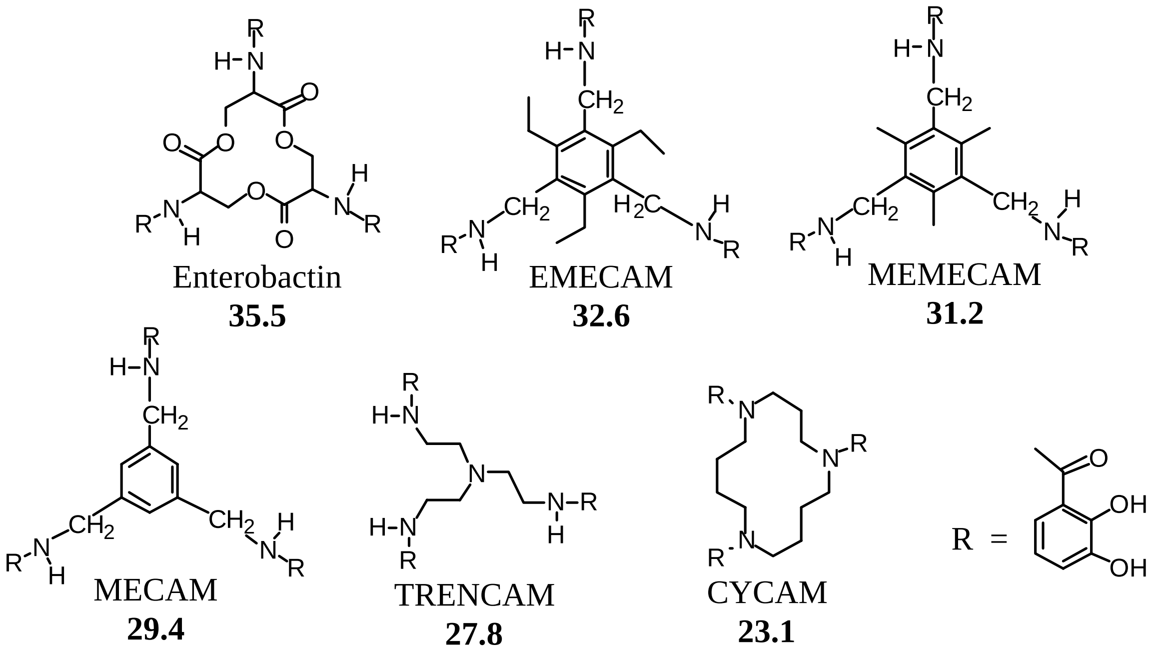
Dissolution studies to date have concentrated on the hydroxamic acid-type ligands with one, two, and three hydroxamate functional groups; acetohydroxamate; rhodotorulic acid; and desferrioxamine B. Batch-type pH-statistics investigations have shown that dissolution rates of iron oxides (geothite, hematite, and magnetite) increase by more than an order of magnitude as the number of functional groups per molecule increase (i.e., acetohydroxamate, rhodotorulic acid, and desferrioxamine B) even though the total concentration of hydroxamic acid groups remain constant. Unlike oxide dissolution in the presence of ethylenediaminetetraacetic acid (EDTA), the iron oxide dissolution rate appears to decrease linearly as pH is increased from 4.5 to 9.0. This suggests that, unlike EDTA, there is limited binuclear adsorption of the ligand or readsorption of the dissolved iron-siderophore at low pH when the surface is positively charged.

An extended molecular mechanics MM3 model has been developed for Fe(III) complexes with catecholamides. Assignment of Fe-O stretch, Fe-O-C bend, and Fe-O-C-C torsion parameters was based on geometries and potential energy surfaces from density functional theory calculations and crystal structure data and were investigated at the MP2 level of theory. These included rotational potential surfaces for several C-C bond types and hydrogen bonds involving phenol. The result models empirical relationships between force constants and physical properties. In addition to these metal-dependent interactions, several unknown intra-ligand interactions reproduce crystal structures with the expected level of accuracy. By changing only the M-O stretching parameters, a good agreement between calculation and experiment is obtained for other metal ions. In addition, we found that this model is applicable to tropolonate complexes. Published barriers to octahedral inversion are reproduced to within ± 2 kcal/mol for $[\mathrm{Al(III)(tropolonate)_3}]$ and $[\mathrm{Ga(III)(catecholamide)_3}]^{3-}$.

Applying this model led to the first quantitative structure-activity relationship for catecholamide ligands. Conformational searches yielded the lowest-energy forms of the six-protonated ligands shown in Figure 1. Conformational searches were also run to identify the lowest-energy forms of their Fe(III) complexes. We obtained the difference in steric energy between the Fe-L complex and the hexaprotonated ligand. A plot of pFe versus this energy difference yields a highly significant linear correlation. The result suggests that this method can be used to screen other candidate architectures for ligands based on the catecholamide donor group.

Planned Activities

Dissolution studies will focus on catecholamide siderophores that have been isolated from selected organisms. In addition, several catecholates are being synthesized to systematically test the MM3 model discussed above. Investigations will continue to focus on the Fe oxides (geothite, hematite, and magnetite). However, studies of UO_2 dissolution will begin at the end of this year and continue in the final year of this project. Modeling efforts will continue to expand to include the hydroxamate siderophores. To date, the optical spectroscopy investigations have not progressed as anticipated but will continue, and these efforts will be integrated with the XAS investigations of S. Traina and S. Myneni.



Enterobactin **35.5**

EMECAM **32.6**

MEMECAM **31.2**

MECAM **29.4**

TRENCAM **27.8**

CYCAM **23.1**

Figure 1. Six Tris-Catecholamide Siderophore Architectures Have Been Examined Using the Developed Model. Relative affinities for Fe(III) are given as pFe values (10 μM ligand, 1 μM Fe(III), and pH 7.4).

Spend Nuclear Fuel and Nuclear Materials

Radiolytic and Thermal Processes Relevant to Dry Storage of Spent Nuclear Fuels

(Project Number: 60392)

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Specific DOE Problem

The project addresses several major DOE/EMSP science needs for the Spent Nuclear Fuel Focus Area: 1) stabilization of spent nuclear fuel, including mechanism of pyrophoricity and combustion parameters for various fuel types, 2) characterization of spent nuclear fuel, 3) development of methods to remove moisture without damage to fuel elements, and 4) characterization of corrosion, degradation, and radionuclide release mechanisms, kinetics, and rates for fuel matrices.

Research Objective

The purpose of this project is to deliver pertinent information that can be used to make rational decisions about the safety and treatment issues associated with dry storage of spent nuclear fuel materials. In particular, we will establish an understanding of: 1) water interactions with failed-fuel rods and metal-oxide materials 2) the role of thermal processes and radiolysis (solid-state and interfacial) in the generation of potentially explosive mixtures of gaseous H_2 and O_2, and 3) the potential role of radiation-assisted corrosion during fuel rod storage.

Research Progress and Implications

Interaction of water vapor with $UO_2(001)$ was studied by using low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), and electron-stimulated desorption (ESD). LEED and LEIS measurements were carried out at Rutgers University and PNNL. XPS and ESD experiments were done at the EMSL facility at PNNL. ESD measurements of clean UO_2 indicate the desorption of H^+ and O^+; the kinetic energy distribution of the latter peaks at 3.5 eV. The O^+ desorption threshold is at 25 eV and is correlated to the ionization of the oxygen 2s level. LEIS, XPS, and ESD results indicate that adsorbed water is completely dissociated on $UO_2(001)$ at 300K and that O atoms are incorporated into the surface. The results also suggest diffusion of oxygen into the bulk.

A high-vacuum chamber has been designed for the experiments with K-West Basin fuel samples being conducted in the radiation-controlled area of PNNL. The new facility is equipped with a low-energy (5-500 eV) electron gun, a high-resolution focused ion gun, and a secondary electron detector and mass spectrometer. This allows secondary electron microscopy imaging, secondary ion mass spectroscopy, and ESD of spent fuel samples from the K-West Basin.

Gamma radiation-induced degradation of water on oxide particle/water interfaces was studied. Thirty powdered ultrapure (>99.99%) crystal oxides were examined. According to the radiation-chemical yield, the oxides can be generally classified into three groups: 1) inhibitors, which lower the H_2 yield, 2) indifferent oxides, and 3) ZrO_2 and some other oxides that increase the H_2 yield more than the radiolysis of pure gas-phase water. A mechanism is proposed for the adsorbed water radiolysis on the ZrO_2 surface, based on the migration of excitons to the surface and their resonant coupling with the H_2O adsorption complex.

Time- and energy-resolved laser-stimulated luminescence (LSL) measurements were used to investigate the dynamics of electronic excitations in ZrO_2. We observe LSL from the decay of three excited states, 2.70, 2.27, and 2.10 eV. The emission kinetics are hyperbolic for all the luminescence bands, which indicates a recombination mechanism. We suggest that recombination primarily involves electrons trapped at intrinsic and extrinsic defect sites and mobilized holes.

The breakdown of zirconia films (important to the integrity of Zr-alloy fuel-rod cladding) under extreme radiation conditions has been systematically studied using low-energy electron and photon bombardment of well-characterized ZrO_2 surfaces. These studies have clarified the mechanism of oxygen removal from such surfaces. This involves ionization of cation core levels, followed by interatomic auger decay resulting and rapid ejection of O+ ions.

Planned Activities

We will submit a renewal proposal to 1) characterize major forms of water physically and chemically bonded to major components of the real SNF samples, 2) investigate radiation-induced gas generation and surface degradation on real SNF samples, cladding and rubble materials containing residual bounded water, and 3) complete the development of a predictive model for the radiolytic gas release from the surface of SNF and other components during “dry” storage.

Information Access

1997-1998 Progress Report. Available URL: http://apollo.osti.gov/em52/1998projsum/60392.pdf

1998-1999 Progress Report. Available URL: http://apollo.osti.gov/em52/1998projsum/60392.pdf

EMSP Workshop, July 1998 Project. Available: http://apollo.osti.gov/em52/1998projsum/60392.pdf

Haustein P. 2000. “Nuclear stimulated desorption studies of oxides relevant to spent fuel material.” *J. Nucl. Mater*. (in preparation).

Hedhili MN, BV Yakshinskiy, and TE Madey. 2000. “Interaction of water with UO_2 (001).” *Surf. Sci*. 445:512-525.

Petrik NG, AB Alexandrov, AI Vall, and TM Orlando. “Gamma radiolysis of water on oxide surfaces: Parameters controlling the energy transfer.” *J. Phys. Chem. B* (in preparation).

Petrik NG, AB Alexandrov, T.M. Orlando, and A.I. Vall. 1999. “Radiation-induced processes at oxide surfaces and interfaces relevant to spent nuclear fuel storage.” *Trans. ANS* 81,101.

Petrik NG, DP Taylor, and TM Orlando. 1999. "Laser-stimulated luminescence of yttria-stabilized cubic-zirconia crystals." *J. Appl. Phys*. 85:6770.

Shutthanandan V, S Thevuthasan, and TM Orlando. 2000. "Hydrogen-damage interactions in yttrium stabilized zirconia." *J. Nucl. Mater*. (in preparation).

Simpson WC, WK Wang, JA Yarmoff, and TM Orlando. 1999. "Photon- and electron-stimulated desorption of O+ from zirconia." *Surf. Sci*. 423:225.

Taylor DP, WC Simpson, K Knutsen, MA Henderson, and TM Orlando. 1998. "Photon-stimulated desorption of cations from yttria-stabilized cubic ZrO_2." *Appl. Surf. Sci*. 101:127-129.

Thevuthasan S, SI Yi, YJ Kim, TT Tran, GS Herman, V Shutthanandan, SA Chambers, CHF Peden, and TM Orlando. 2000. "Surface structure determination of Y-ZrO_2(001) using mass separated recoil spectroscopy and x-ray photoelectron diffraction." *Surf. Sci*. (in preparation).

Distribution and Solubility of Radionuclides and Neutron Absorbers in Waste Forms for Disposition of Plutonium Ash and Scraps, Excess Plutonium, and Miscellaneous Spent Nuclear Fuels[a]

(Project Number: 60387)

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(a) This title has been shortened from that of the proposal for brevity and clarity.

Research Objective

Successful immobilization of actinides (Am, Cm, Th, Pu, Np, etc.) in crystalline and amorphous host matrixes with appropriate neutron absorbers (B, Hf, Gd, etc.) requires sound scientific knowledge of the local chemical environments of both the actinides (An) and the neutron absorbers and their interaction with the host matrixes. This understanding leads to a more systematic and efficient approach to predicting solubilities than the strictly empirical approach now used. The goals of this ongoing research are to determine solubility limits of representative actinides (Pu and U) and neutron absorbers (Hf and Gd) in crystalline and amorphous matrixes and to determine solution mechanisms of these species in the two types of systems. Actinides and neutron absorbers in amorphous systems have been studied at PNNL in collaboration with LBNL and University of Michigan and in crystalline systems at ANSTO. We believe that we are in a position to understand the chemical systematics of silicate melts so that the solubility of actinides, neutron absorbers, and, we would suggest, other metal species in glass no longer must be determined empirically but can be calculated from a set of equilibrium constants in a fashion similar to aqueous systems.

Research Progress

For the first time, to the best of our knowledge, we have demonstrated in amorphous systems that at least 14.7 mol% Pu(III) plus 4.2 mol% Gd(III) is soluble in an alkali boro-aluminosilicate glass under reducing conditions. Under oxidizing conditions, considerably less Pu(IV) is soluble. X-ray absorption fine structure (XAFS) analyses of these glasses, performed at LBL, confirm that Pu(III) is a dominant species in the reduced glass and Pu(IV) in the oxidized glass.

The solution behavior of lanthanides [Ln(III)]: Ln = Gd, La, and Nd) in a variety of Na_2O-Al_2O_3-B_2O_3-SiO_2 glasses was studied with a host of complementary analytical techniques. Results from experiments with the lanthanides Gd, Nd, and La suggest that their behavior in the glass melt is similar. The solution behavior of Ln in these glasses was determined by the ratio of excess Na_2O or excess Al_2O_3-to-B_2O_3 in the melt.

In peralkaline melts ($Na_2O>Al_2O_3$), when the ratio of excess Na_2O (i.e., moles of Na_2O less the moles of Al_2O_3) to B_2O_3 is greater than 0.5, the compound $Na_xLn_{9.33-0.33x}Si_6O_{26}$ ($0<x<1$) precipitates from the melt at the Ln_2O_3 solubility limit. The Ln_2O_3 solubility in these glasses is determined by the concentration of each glass former. From the ultraviolet-visible (UV-Vis) and fluorescence spectroscopy results, lanthanides appear to dissolve uniformly at low concentrations in these glasses. When the B/Ln ratio is ≥3, intermediate range-ordered Ln-borate structural groups appear to form in clusters about 5 nm in diameter. The electron energy loss fine structure (ELFS) results suggest that the structure of these Ln-borate groups resembles lanthanide metaborate crystals. When B/Ln is less than 3, Ln appeared to partition among boron-rich and silicon-rich domains, forming different types of intermediate-ordered structural groups. The configuration of these groups has yet to be determined.

When the ratio of excess Na_2O to B_2O_3 is less than 0.5 in these glasses, liquid-liquid phase separation occurs above the Ln_2O_3 solubility limit with one phase rich in Ln and B. The Ln_2O_3 solubility appears to be determined by the excess Na_2O. In these glasses, the borate and silicate portions are not well mixed. Phonon side band spectroscopy results suggest that Ln is incorporated into the borate portion of the melt in a double chain structure similar to that in lanthanide metaborate. The Ln behavior in peraluminous melts (moles of $Al_2O_3>Na_2O$) is similar to the behavior in peralkaline melts. When the excess $Al_2O_3/B_2O_3 < 0.4$, phase separation occurs at the solubility limit of Ln_2O_3 with one phase rich in Ln and B. When the excess Al_2O_3/B_2O_3 is greater than 0.4, $Na_xLn_{9.33-0.33x}Si_6O_{26}$ precipitates above the Ln_2O_3 solubility limit.

Based on the assumption that the Pu(III) and Ln(III) solution behaviors are similar in these glasses, we anticipate that Pu(III) dissolves in glass in much the same way as Ln(III). Above Ln solubility in some glasses, $Na_xLn_{9.33-0.33x}Si_6O_{26}$ crystallizes from the melt. If this crystal accommodates significant quantities of Pu(III), the resulting glass ceramic could also be an acceptable waste form.

In contrast to the Gd results, at all concentrations up to the solubility limit, XAFS results indicate that Hf(IV) dissolves in these glass melts as (HfO_6), octahedrally coordinated species in peralkaline glasses and less-than-octahedral in peraluminous glasses without clustering (Hf-O-Hf bonds). In our glasses, HfO_2 solubility is observed to reach a minimum for glasses in which the molar concentrations of Na and Al are equal. Limited increases in Al_2O_3 result in glasses (peraluminous) with slightly increased Hf solubility. Further increases in Al_2O_3 result in glasses that can no longer be melted at 1550°C. When the Na_2O-to-Al_2O_3 ratio is greater than 1 (peralkaline glasses), there is an increase in the HfO_2 solubility with an apparent increase in the Na_2O content. Results from XAFS suggest that the local structure around Hf is silicate-like for peralkaline glasses and siloxane-like for peraluminous glasses (i.e., the local structure is different for the two glass types). A comparison between the coordination environments of Pu(IV) and Hf(IV) is under way. The anticipated results from this study may suggest that An(IV) dissolves in these glass melts as monomeric species.

Compositional effects on HfO_2 solubility are being studied extensively in these glasses. We have been able to model the HfO_2 solubility in these glasses with a rule-of-mixtures approach using the measured HfO_2 solubility in rudimentary compositions such as amorphous analogs of sodium disilicate, sodium diborate, albite, and reedmergnerite. From such a modeling approach, we find that the highest HfO_2 solubility occurs in glasses containing the highest concentration of "$NaBO_2$" stoichiometric units, perhaps indicating that the chemistry of Na and B in the silicate melt is the determining factor for HfO_2, and perhaps An(IV), solubility.

For the candidate ceramic host matrixes, substitution of Pu, U, Hf, and Gd in the host structures is now quantified and broadly understood in terms of the standard rule that the closer the sizes (~15% difference) of the guest and host ions, the higher is the solubility of the guest ions. In the current study, solid solubility limits, in formula units (f.u.) of U, Pu, Hf, and Gd, have been measured for single actinides and neutron absorbers. The matrixes were zircon ($ZrSiO_4$), monazite ($CePO_4$), titanite ($CaTiSiO_5$), perovskite ($CaTiO_3$), and apatite

($Ca_{10}(PO_4)_6O$). In almost all cases, these limits were not known before this study. Uranium (IV) is highly soluble in apatite achieving 0.5 f.u., while 8 f.u. of Gd is soluble. However, very limited solubility was found for Hf (< 0.1 f.u.). Titanite was observed to accommodate 0.02 f.u. of U(IV) and 0.02 f.u. of Pu(IV), both of which substitute for Ca. At solubility, UO_2 or PuO_2 form. Under reducing conditions, a higher solubility of Pu (0.05 f.u.) as Pu(III) was determined. The use of an argon atmosphere rather than air during sintering of these materials presumably causes Pu(III) to form instead of Pu(IV). Relatively large accommodations of neutron absorbers were observed in titanite, 0.3 f.u. of Gd in the Ca site and 0.5 f.u. of Hf in the Ti site. Plutonium has high solubility in monazite as Pu(IV) at up to 1 f.u (at firing temperatures of < 800ºC) and Pu(III) at 1 f.u., although there is almost no solubility for Hf (<0.01 f.u.). Perovskite accommodates high concentrations of the neutron absorbers Gd or Hf at 1 f.u. and Pu(III) at 1 f.u., but limited amounts of Pu(IV) (0.13 f.u.) and U(IV) (~0.1 f.u.). Previous studies showed that actinides and neutron absorber solubilities are high in zirconolite, 0.7 f.u. for U(IV) and Pu(IV) and 1.4 and 1 f.u. for Gd and Hf, respectively. In pyrochlore, the solubilities were known from previous studies to be 1, 2, 1, 2 and 0.3 f.u. for U(IV), Pu(III), Pu(IV), Gd, and Hf, respectively.

Using the new insight into the Pu, Gd, and Hf behavior in crystalline materials and glass melts, we have identified optimum formulations to incorporate the maximum amount of Pu. Studies are under way to validate these predictions. For crystalline materials, site substitution and charge compensation mechanisms of the actinides and neutron absorbers will be studied further. Interactive effects of actinide and neutron absorbers on their solubilities in both glasses and ceramics will be studied. In particular for glasses, we feel this approach can be extended to other metal species with the ultimate goal to develop a comprehensive model for silicate melts and glasses in which chemical systematics are well defined.

Soil and Groundwater Cleanup

Mineral Surface Processes Responsible for the Decreased Retardation (or Enhanced Mobilization) of ^{137}Cs from HLW Tank Discharges

(Project Number: 27617)

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Problem Addressed

The project investigates cesium geochemistry in Hanford sediments under chemical conditions relevant to high-level waste (HLW) single-shell tank (SST) leakage. Fundamental information developed by the research will be useful in assessing the long-term risk posed by massive in-ground concentrations of ^{137}Cs in the Hanford tanks farms and in establishing scientifically credible closure plans. Project research results are now being used in improved reactive transport models to simulate cesium migration in the vadose zone beneath leaked SSTs in the S-SX tank farm at Hanford.

Research Objective

Experimental research will determine how the sorption chemistry of cesium on Hanford vadose zone sediments changes after contact with solutions characteristic of HLW from SSTs. Our central hypothesis is that the high ionic strength of tank wastes (i.e., >5 mol/L $NaNO_3$) will suppress all surface-exchange reactions of cesium except those to the highly selective frayed edge sites (FES) of the micaceous fraction. We further speculate that the concentrations, ion selectivity, and structural aspects of the frayed edge sites will change after contact with the harsh chemical conditions of HLW and that these changes will be manifest in the macroscopic sorption behavior of cesium. We believe that migration predictions of cesium can be improved substantially if such changes are understood and quantified.

Research Progress and Implications

Key accomplishments of this research are as follows:

- Cesium sorption to Hanford sediment has been found to be a sensitive function of sodium concentration up to saturation with $NaNO_{3(s)}$. High sodium swamps all sorption sites except high-affinity ones on micas. Contrary to conventional wisdom, Na^+ and Cs^+ compete for high-affinity micaceous frayed edge sites. Cesium migration is greatly expedited in $NaNO_3$ brines where K_d's can approach 0.

- The FES sites are associated primarily with biotite and vermiculitized biotite and not muscovite. Microbeam analyses (electron microprobe, synchrotron x-ray microprobe) of cesium-containing micas documented cesium accumulation at specific areas on crystallite edges and in microscopic internal channels associated with weathering planes and physical fractures.

- A multiple-site, multicomponent surface complexation model for cesium adsorption to Hanford sediments has been developed for Na^+, Ca^{2+}, and K^+ electrolytes. The model extends over the electrolyte concentration range found in dilute, concentrated, and self-boiling HLW tanks and is suitable for linkage with a transport code.

- Cesium sorption extent increases with both temperature and OH^- content of the aqueous phase. Higher base concentrations (e.g., >1.0 mol/L) and temperature (e.g., 50°C) promote oxidation and expansion of biotite crystallites, increases in cation exchange capacity (CEC), and surface precipitation/armoring of the mica sorbents by Fe(III) oxides.

- Techniques for the isolation, identification, and counting of ^{137}Cs-containing mineral particles in contaminated sediment have been developed and refined by application to a single HLW-contaminated subsurface sediment collected from beneath leaked tank SX-109 at Hanford (10^5 pCi/g ^{137}Cs). The Cs-containing particles were primarily biotite, and the sorbed Cs was strongly resistant to desorption.

Planned Activities

Our final experimental campaign is investigating the combined impact of high OH^- and $Al(OH)_4^-$ on Cs^+ adsorption by Hanford vadose zone sediments over a temperature range of 35° to 95°C relevant to the subsurface discharge of self-boiling Redox[(a)] wastes. Experiments are tracking the concurrent dissolution of sorbing micaceous minerals and precipitation of aluminum oxides and the impact on cesium adsorption and fixation by the sediments. We are also working to finalize three other publications that have resulted from past research.

Information Access

Zachara JM, SC Smith, JP McKinley, RJ Serne, C Liu, and PL Gassman. 2000. "Sorption of Cs^+ to Micaceous Subsurface Sediments from the Hanford Site, Washington." *Clays and Clay Minerals* (submitted).

McKinley JP, RJ Serne, JM Zachara, CJ Zeissler, and RM Lindstrom. 2000. "The Distribution and Retention of ^{137}Cs in Sediments Beneath Leaked Waste Tanks at the Hanford Site, Washington." *Environmental Science and Technology* (submitted).

(a) Redox refers to wastes at Hanford derived from the REDOX process. In the process aluminum-clad fuels and zircaloy-clad fuels were declad. Redox waste is the high-level component of these manipulations.

Rapid Migration of Radionuclides Leaked from High-Level Waste Tanks: A Study of Salinity Gradients, Wetted Path Geometry, and Water Vapor Transport

(Project Number: 65410)

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Problem Statement

Previous attempts to predict field-scale contaminant transport through the vadose zone at the Hanford Site have often neglected driving forces and mechanisms that are known to contribute to preferential flow. It is now clear that a basic understanding of the behavior of dense high ionic-strength fluids through the vadose zone is critical to the evaluation of remediation options and for predicting future migration. Preferential flow has been shown to be capable of producing erratic transport patterns and can cause contaminants to bypass much of the unsaturated soil matrix. These processes lead to fast transport of contaminants to underlying groundwater and the resulting lack of interchange between the main soil matrix and the fast pathways reduces the potential for natural attenuation. Our hypothesis is that elevated surface tension and density of leaked tank wastes will lead to the formation of narrow fingers of infiltration, reducing lateral contaminant spreading, and increasing the depth of penetration. The extent and persistence of these fingers will be influenced by natural precipitation as well as water migrating into the saline zone in response to the osmotic potential gradient.

Research Objectives

This study combines laboratory, field, and numerical experiments with the following objectives: to investigate the effect of elevated surface tension, density, and viscosity of highly saline fluids on soil water-retention properties, wetting front instability, the formation and persistence of fingers, and contaminant mobility to investigate the conditions under which osmotically driven vapor flux is operative and quantify its impact on plume transport to develop and incorporate a theory describing these processes into an existing DOE-developed, numerical simulator to allow prediction of contaminant migration at realistic spatial and temporal scales. The product will be a tool that DOE can use to perform more realistic analyses to predict fate and transport of high ionic-strength contaminants, evaluate different tank waste retrieval strategies and their impact on the vadose zone, and assess the associated health risks.

Research Progress

The report summarizes work after 16 months of a three-year project that started in October 1998. As of February 2000, under the controlled laboratory experiments tasks, we have successfully demonstrated the formation of fingers during the infiltration of concentrated tank waste simulants. We have been successful in demonstrating the utility of x-ray computed tomography (XRCT) for monitoring 3-D finger evolution in Hanford sediments.

Studies in 2-D light chambers have also produced good results so far. Studies were performed with pure 5-M $NaNO_3$ and with $NaNO_3$ + 2% methanol by volume designed to maintain the density and viscosity effects while reducing the surface tension to a value similar to water. A variety of well-characterized silica sands are being used in this study to allow identification of the dominant mechanisms. Figure 1 shows the results at four different times for the application of three 5-mL plumes in 30/40 Accusand®. The plumes consisted of 5 M $NaNO_3$,

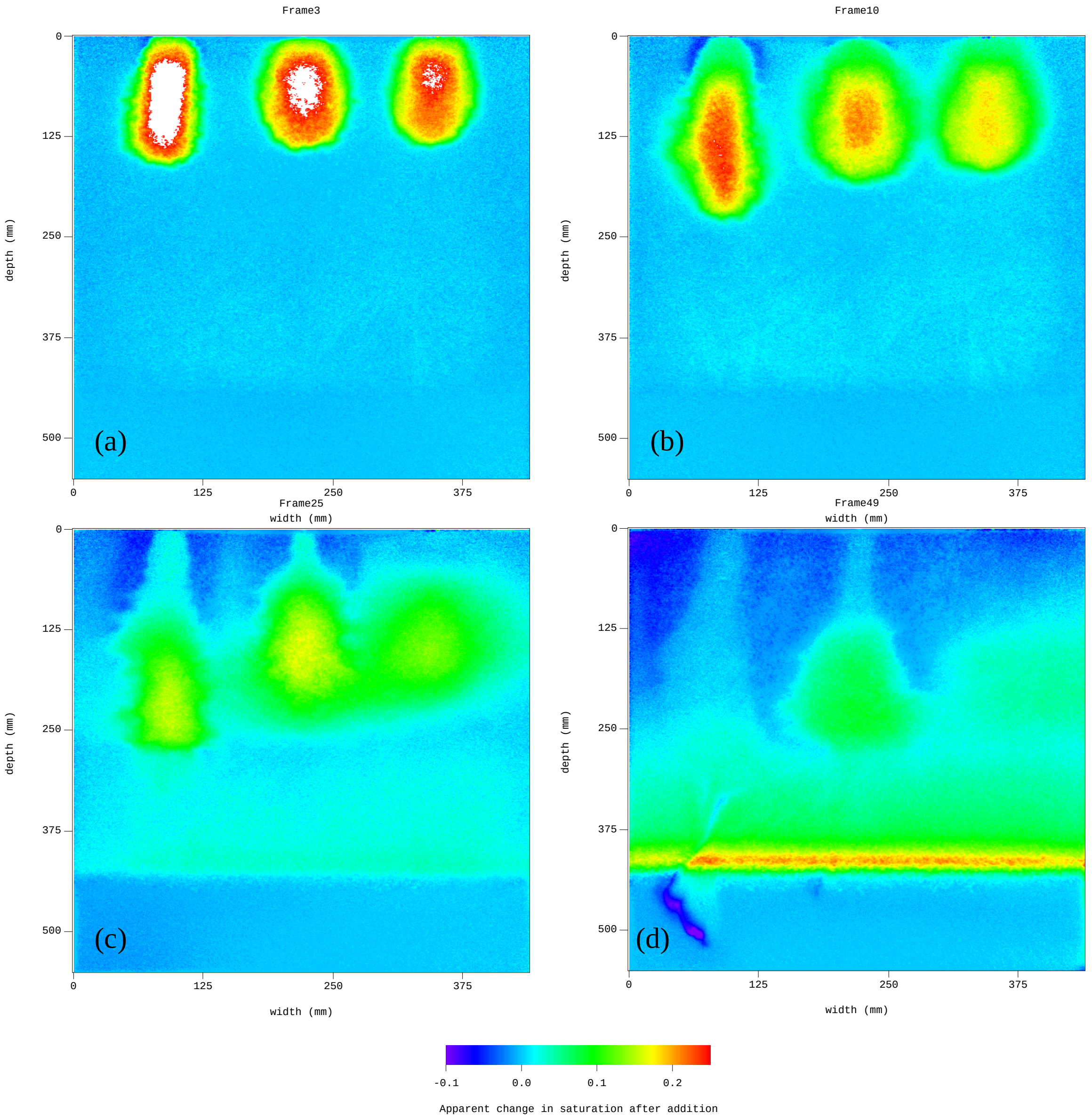

Figure 1. Infiltration Patterns of 5-mL Pulse of Concentrated Solutions Into 30/40 Accusand; (a) After 0.5 Hr of Infiltration, (b) After 1.6 Hr of Infiltration, (c) After 10 Hr, and (d) After 64 Hr. The solutions applied were (from left to right): 5 M $NaNO_3$, 5 M $NaNO_3$ + 2% methanol by volume, and Nanopure® water.

5 M $NaNO_3$ + 2% methanol by volume, and distilled water (from left to right). The salt plume (left) clearly infiltrated faster than the other two plumes, despite the similarity in densities between the left two plumes. It appears that the high surface tension of the salt plume is responsible for the higher velocity. The effect of the osmotic gradient is also clear. The darker blue regions on the figure indicate water saturation below levels present before the addition of the plumes (see color table at the bottom of the figure). Desaturation of areas adjacent to both

salt fingers continues throughout the experiment. In addition, at a later time (~ 10 hr), water from the right plume was being drawn into the adjacent salt plume. This is likely in response to the osmotic gradient between the two plumes. Another interesting phenomenon observed in the later stages of the infiltration experiment (~ 60 hr) is the mobilization of colloids. Soon after the salt plume reached the capillary fringe (375–400 mm depth) reddish “tail,” apparently colloidal materials, developed and moved down toward the bottom of the chamber (density driven). The tail was also observed below the salt plume with 2% methanol but was less pronounced.

Under the modeling task, we have been successful in developing and implementing thermodynamic based model of surface tension as a function of ionic composition. The model uses the Pitzer equations to predict osmotic coefficients from which surface tensions can be derived for concentrated aqueous solutions. The resulting model has been used to scale the hysteretic water retention and hydraulic conductivity relations to predict the effects of tank waste on soil hydraulic properties and infiltration processes. As the concentration of salt in the fluid increases, the surface tension increases and wettability decreases, causing an arrest of spontaneous imbibition. This condition is known to cause finger formation in water-repellant soils. Another important achievement has be the start of work on the incorporation of adaptive gridding techniques into the STOMP simulator to allow tracking of fingers from their formation at the local scale through their development over larger spatial scales. The approach is based on static local uniform grid refinement method that integrates on nested sequences of local uniformly refined Cartesian grids. This will overcome current limitations on our ability to track fingers at realistic scales after their formation.

Planned Activities

During the remainder of this fiscal year, laboratory experiments will continue to measure the effect of ionic composition on fluid properties and to characterize the effect of concentrated electrolyte solutions of water retention and hydraulic conductivity relationships. These results will be used to validate the theory developed to describe the effects. Work is ongoing to collect laboratory data to verify the predicted surface tensions and observed changes in constitutive properties. An apparent difference in effect on the imbibition and desorption curves will be explored in the coming months. Tank waste simulants will be used in intermediate-scale flow cells packed with Hanford sediments to observe the infiltration of tank waste simulants under controlled conditions and identify the conditions under which fingers form and factors affecting their persistence. The light chamber studies will continue with some emphasis on identifying the conditions under which colloids are mobilized and how they impact transport to the water table. Another field experiment to observe in situ infiltration and transport behavior in Hanford formation soils will be conducted this summer, while monitoring of the long-term plume migration experiment continues. These studies will provide data for validation of model predictions at the field scale.

Technetium Attenuation in the Vadose Zone: Role of Mineral Interactions

(Project Number: 70177)

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Research Objective

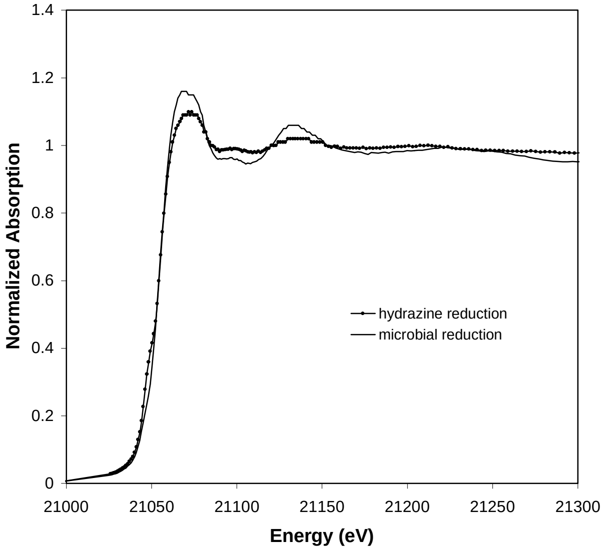
This research project will provide fundamental information on surface-mediated reduction/ precipitation reactions of Tc on Fe^{II}-containing mineral surfaces and the stability of those precipitates under conditions relevant to the vadose zone at the Hanford Site.

Our strategy is to 1) develop a mechanistic description of surface-mediated reduction of Tc^{VII} on Fe^{II}-containing minerals, 2) determine the stability of the precipitated Tc^{IV} solids, and 3) validate our model of Tc attenuation using contaminated Hanford Site sediments. This information will provide crucial support for the development of models of contaminant mobility in the vadose zone. With reliable models, a major cost reduction in remediation efforts may be achieved by targeting those sites that present the greatest environmental threat.

Research Progress and Implications

This report summarizes progress after six months of a three-year project. We have made progress in the areas of TcO_2(am) solubility studies; TcO_2(am) was prepared from pertechnetate stock solution by hydrazine and microbial reduction using the subsurface dissimilatory iron-reducing bacterium, *Shewanella Putrefaciens*. The amorphous product prepared by both methods was characterized by x-ray absorption spectroscopy and x-ray diffraction at Stanford. In Figure 1, the near-edge structure of the x-ray absorption spectra indicates complete reduction of Tc^{VII} to Tc^{IV} by either method. Note, however, that the amplitude of the extended x-ray absorption fine structure (EXAFS) of the microbially reduced TcO_2(am) is significantly greater than the hydrazine reduced result TcO_2(am). This is especially evident in the k^3-weighted EXAFS spectra shown in Figure 2 and in the Fourier transforms of the EXAFS spectra shown in Figure 3. Fits to the EXAFS indicate that the first and second shells in the Fourier transform correspond to oxygen and technetium atoms, respectively. The decreased EXAFS amplitude of the hydrazine-reduced TcO_2(am) may result from increased static disorder; however, this needs to be confirmed by additional experiments.

Even though the product of the hydrazine and microbial reduction is an amorphous collection of the x-ray diffraction spectrum (Figure 4), it is still meaningful through analysis of the pair distribution function. From these analyses, the radial distribution of all the atom pairs in the material can be determined yielding longer-range structural information than can be determined from analysis of the x-ray absorption spectra. By comparing the pair distribution function of TcO_2(am) produced by hydrazine and microbial reduction, one can validate the increased static disorder suggested by the x-ray absorption measurements.



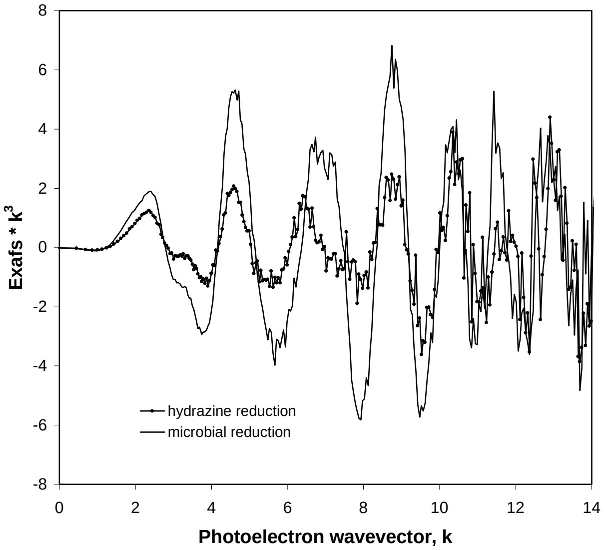
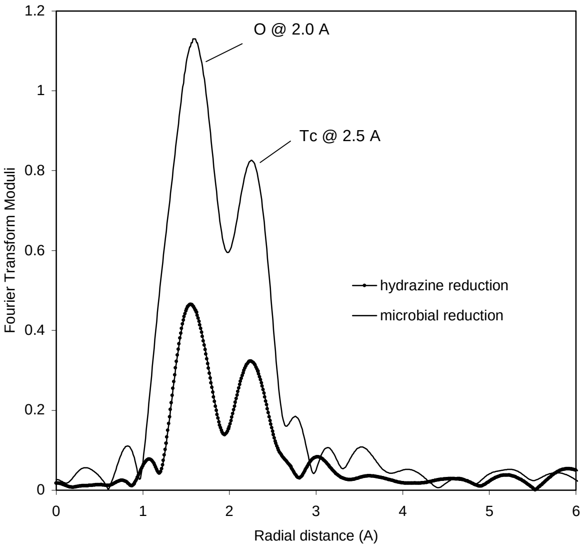


Figure 1. Near-Edge Spectra Showing Complete Reduction of TeVII to TeIV

Figure 2. K3-Weighted EXAFS Spectra



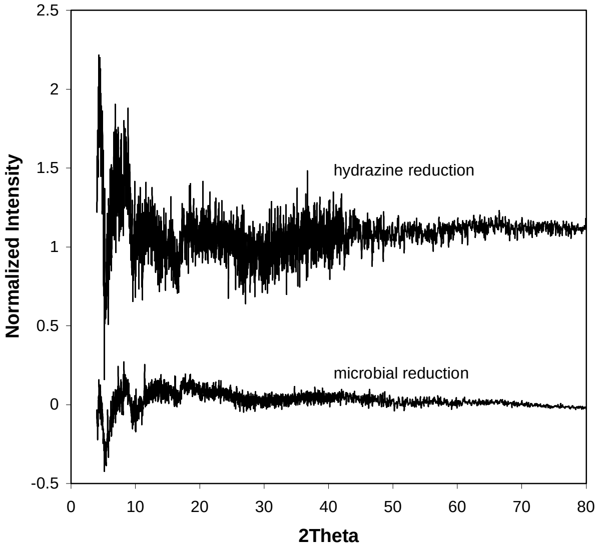


Figure 3. Fourier Transform of EXAFS Spectra

Figure 4. X-Ray Diffraction Spectrum

Planned Activities

The solubility of TcO_2(am) and possible Tc^{IV}-Fe^{III} oxides will be measured as a function of pH under rigorously controlled redox conditions. The oxidation state of Tc in solution will be determined at PNNL by a variety of methods such as solvent extraction, laser photoacoustic spectroscopy (LPAS), ultraviolet-visible (UV-Vis), and near infrared (NIR) spectrophotometry, and x-ray absorption near-edge structure (XANES) analysis will be carried out at the Stanford Synchrotron Radiation Laboratory. The methods used will depend on the concentration of Tc in solution. Solvent extraction and LPAS will provide oxidation state information at the lowest Tc concentrations, approximately 1×10^{-9} M. The solvent extraction process requires acidification of the sample that can potentially change the oxidation state. On the other hand, LPAS requires no alteration to the solution chemistry and distinguishes between the reduced Tc oxidation states. But LPAS is very time-intensive. The detection limits for UV-Vis-NIR spectrophotometry and XANES analyses are approximately 1×10^{-6} M and 5×10^{-4} M, respectively.

Solubility experiments are also planned on Tc-contaminated minerals isolated from vadose zone sediments at Hanford. Ideally, these contaminated sediments will be obtained from the discharge sites associated with the B Plant, where the highest Tc-contaminated fluids were released. Simulated Tc-contaminated samples will be made with selected Hanford Site sediments that have demonstrated retention of Tc (Plio-Pliestocene and upper Ringold Formation). These sediments will be exposed to TcO_4^- solutions for extended periods of time under saturated and unsaturated conditions in an oxic environment.

The Influence of Calcium Carbonate Grain Coatings on Contaminant Reactivity in Vadose Zone Sediments

(Project Number: 30952)

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Problem Addressed

The research is addressing vadose zone geochemical processes operative beneath cribs, disposal trenches, retention basins, and leaked high-level waste tanks at DOE sites where calcareous subsurface sediments exist. Project results will allow development of improved reaction-based transport models for vadose zone waste sites at Hanford, INEEL, and other DOE facilities. Fundamental insights will be provided on reaction mechanisms responsible for contaminant retardation and immobilization in the vadose zone that will support scientifically defensible decisions on site remediation and closure, such as the advisability of leaving contaminants in place.

Research Objective

In this newly awarded project, fundamental research will determine the role of calcium carbonate grain coatings on the vadose zone chemical reactivity of key Hanford contaminants (i.e., $^{60}Co^{2+}$, $^{90}Sr^{2+}$, CrO_4^{2-}, and $^{99}TcO_4^-$). Calcium carbonate is widely distributed through the Hanford vadose zone as a result of current and past geochemical processes and exists as grain coatings and intergrain fill. We hypothesize that carbonate coatings enhance the sorption of carbonate compatible contaminants (e.g., ^{90}Sr, ^{60}Co) through adsorption and coprecipitation processes but interfere with the reductive immobilization of the oxoanions CrO_4^{2-} and TcO_4^- by passivating electron dense surfaces of Fe^{2+} minerals such as magnetite and biotite in Hanford sediments. The research is investigating the behavior of calcium carbonate grain coatings, including how they form and dissolve, their reactivity toward contaminants under water-saturated and -unsaturated conditions, their impact on the reactivity of the mineral substrate, and their in-ground composition and minor element enrichment. Modern techniques, including x-ray absorption spectroscopy, scanning probe microscopy, and photoelectron spectroscopy, will be applied in concert with carefully selected model systems to provide a rigorous molecular and microscopic understanding of the surface reactivity of carbonate-coated mineral surfaces. Model system studies will be linked with parallel spectroscopic, microscopic, and macroscopic investigations of calcareous Hanford sediments, to provide basic scientific information for the remediation/closure of contaminated sites at Hanford and other DOE facilities.

Research Progress and Implications

This project resulted from the FY 1999 EMSP vadose zone call, and research activities began in FY 2000. The following represent accomplishments from our first four months of research.

- Two post-docs and two graduate students have been recruited to work on the project and have initiated research.

- Thin layers of $CaCO_{3(s)}$ have been reproducible grown on a cut/polished magnetite (111) surface from aqueous solution. The layers have been characterized by electron microscopy and x-ray absorption spectroscopy (Ca-L edge) and found to be the aragonite polymorph. The $CaCO_{3(s)}$-coated magnetite has been reacted with CrO_4^{2-}, and the coating has been found to partially passivate the magnetite surface against CrO_4^{2-} reduction.

- We have imaged step motion on calcite and other carbonate surfaces as a function of pH. This was deemed important because it was found that etch pit shapes are a strong function of pH, and it was thus apparent that great care just be taken in separating the effects of adsorbates such as Co from the effects of pH. Indeed, it is possible that previous studies of alterations in step orientation attributed to the adsorption of organic molecules might be explained simply by the dissociation of the organic acid used and thus to pH effects. We have done further high resolution imaging of steps, and it remains clear that what we call “acute” steps are atomically much straighter than “obtuse” steps near equilibrium. However, the step energies implied by our results are smaller than those of other studies.

- Two different types of calcareous vadose zone sediments have been obtained from a borehole near the S-SX tank farm at Hanford. The first sediment is coarse-textured one from the Hanford formation containing $CaCO_{3(s)}$ coated coarse sands and gravels. The second sediment is from the Plio-Pliestocene contact and contains silty-sand with calcite intergrain and pore fillings. The $CaCO_{3(s)}$ fraction in these sediments is being characterized by various types of beam microscopies to determine morphology, major and minor element composition, co-associated mineral phases, and crystallinity.

Planned Activities

Research over the remainder of the year will continue along the lines described and will emphasize 1) the growth and reactivity of $CaCO_{3(s)}$ coatings of defined thickness on substrates that are representative of reactive mineral phases in the Hanford vadose zone, including magnetite and biotite; 2) the influence of the target contaminants and pH on calcite surface growth features where contaminants associate; and 3) the composition, characteristics, and reactivity of natural $CaCO_{3(s)}$-coated mineral material from the Hanford vadose zone.

The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica Species to High Concentration: Effects on Neutralization of Leaked Tank Wastes and Migration of Radionuclides in the Subsurface

(Project Number: 30944)

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Problem Addressed

The presence of a wide range of radionuclides, metal ions, inorganic ligands, and organic chelating agents combined with the high base and electrolyte concentration in the Hanford waste tanks creates some unique and difficult problems in modeling the aqueous thermodynamics of these solutions. Solving these problems is important since this can lead to better strategies for tank processing and predictions of subsurface transport. In addition, a large number of scientists and engineers at Hanford and other sites rely on these models for making accurate predictions of tank chemistry.

Research Objective

In developing accurate thermodynamic models for these solutions, one of the most important factors is identifying the aqueous species that are present. Identifying these species in tank solutions presents some difficult challenges because 1) current analytical methods for examining speciation in simple solutions, such as ultraviolet-visible (UV-VIS), Raman, and the like, develop difficulties in interpreting or analyzing spectral features when multiple complexes are present and contribute to the observed spectra; 2) the solubility of the compounds of many elements, including the actinide elements, is very low under high base conditions. Determining the aqueous speciation in such solutions, which is still needed to predict changes in solubility, is now done largely by curve-fitting solubility data to hypothesized speciation schemes. Clearly, new and improved approaches to this problem are needed.

Research Progress

In order to circumvent these difficulties we have implemented a comprehensive approach involving coupled experimental solubility studies, spectroscopic measurements of solution speciation, molecular modeling studies that yielded information on species structure and energetics, and thermodynamic modeling efforts using the Pitzer thermodynamic model (which is valid to high ionic strengths). In developing this approach, we have classified the speciation reactions in tank solutions into three areas: simple inorganic speciation reactions involving the addition of one or more ligands to a metal center, organic chelate binding to a metal center where the chelate completely/incompletely wraps the metal center, and systems where the binding ligand polymerizes, forming multiple species that can interact with the metal ion. Examples of each of these types of reactions that affect waste tank and vadose zone applications for the actinides or fission products are described below.

The most important simple inorganic speciation reactions that can occur in these solutions involve the addition of multiple hydroxyl (owing to the high base concentration) or carbonate ligands to the metal center. For example, the addition of one carbonate ligand to the Sr^{2+} cation can result in an asymmetric complex with a strong dipole moment. Under lower base conditions, water molecules bind to the positive part of the dipole (i.e., the Sr ion) to partially neutralize the charge asymmetry. Under higher base or carbonate concentration, these water molecules are replaced with either additional carbonate ligands or hydroxyl groups. In the case of Sr, hydroxyl association is very weak, and the speciation is dominated by carbonate complexation. In the case of more hydrolyzable metal ions, such structural asymmetries can result in mixed complex formation. However, for larger multifunctional group organic chelates such as ethylenediaminetetraacetic acid (EDTA) or N-Hydroxyethylethylenediaminetriacetic acid (HEDTA), the chelate cannot completely surround the metal center (Figure 1), which then becomes associated with hydroxyls at high base concentration. This results in the formation of metal-chelate-hydroxyl complexes that can increase the solubility of trivalent actinide compounds by orders of magnitude in basic conditions. An example of this effect is shown in Figure 2 for the solubility of $Eu(OH)_3$(c), a trivalent actinide analog. The formation of a stoichiometric $EuOHEDTA^{2-}$ species increases the solubility by 2 to 3 orders of magnitude over predictions using a simple EuEDTA species. These increases in solubility and changes in speciation can dramatically affect tank processing strategies because the desire is to retain the actinides and fission products in the sludges rather than develop costly removal strategies.

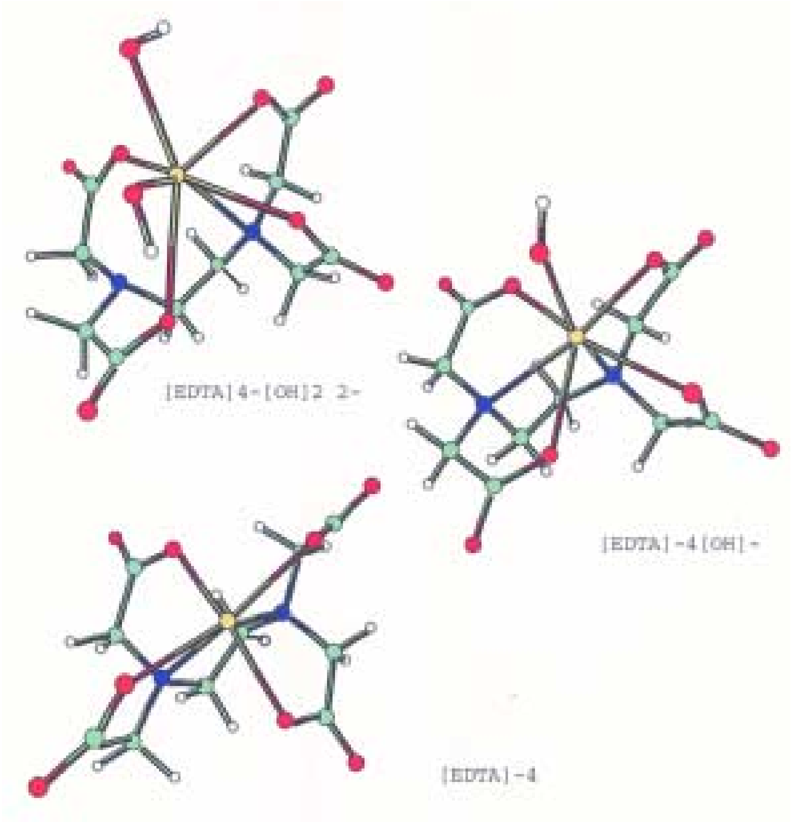

Figure 1. La-EDTA-OH Clusters Exhibiting the Location of OH Groups in the Complexes

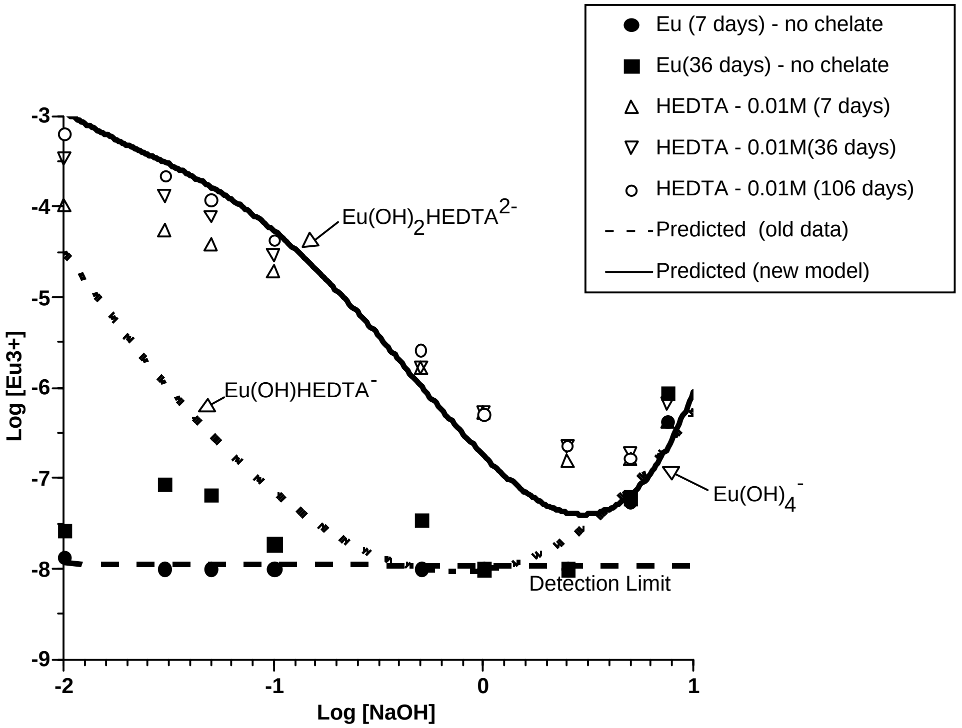

Figure 2. The Effects of Eu-EDTA-OH Complexation on $Eu(OH)_3$ Solubility at High Base

The third major type of speciation reaction involves a ligand which itself can polymerize in solution. The polymerization of the ligand results in several anionic species being present in solution simultaneously. An example of this type of ligand is silica, which can form monomers, dimers, trimers, and tetramers in solution. All of these species have unique binding capabilities and complexation constants with different radionuclides. This is an active area of research wherein unique structural probes such as NMR can distinguish the effects of cation binding to each individual complex. This specific case of silica complexation has relevance to both tank processing and vadose zone issues. Silica complexation is relevant to the vadose zone because the high base concentration, which can result from a tank leak, can dissolve silica-containing minerals in the soil, creating high dissolved silica concentrations. This dissolved silica can then form strong aqueous complexes with fission products and actinides, facilitating their transport through the subsurface.

Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone

(Project Number: 70088)

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Research Objectives

Immobilization of toxic and radioactive metals (e.g., Cr, Tc, U) in the vadose zone by in situ gaseous reduction (ISGR) using hydrogen sulfide (H_2S) is a promising technology being developed by the U.S. Department of Energy (DOE) for soil remediation. Earlier laboratory studies have shown that Cr(VI) in a number of soil samples can be effectively immobilized by treatment with diluted H_2S. A field test has also been completed that resulted in 70% immobilization of Cr(VI). Nevertheless, detailed reaction kinetics and mechanisms for Cr(VI) immobilization are unknown in the H_2S treatment of the vadose zone. The reaction products have not been fully characterized. The long-term metal stability after the ISGR treatment is not fully understood.

The objective of this project is to seek basic scientific understandings concerning the kinetics and mechanisms of interactions among H_2S, the metal contaminants, and soil components. Within the three-year period of this project, the following specific research tasks will be accomplished:

1. evaluation of the potential catalytic effect of mineral surfaces on the rate of Cr(VI) reduction by H_2S and the rate of H_2S oxidation by air

2. identification of the reactions of soil minerals with H_2S and determination of associated reaction rates

3. evaluation of the role of soil water chemistry on the reduction of Cr(VI) by H_2S

4. assessment of the reductive buffering capacity of H_2S-reduced soil and the potential for emplacement of long-term vadose zone reactive barriers

5. evaluation of the potential for immobilization of Tc and U in the vadose zone by reduction and an assessment of the potential for remobilization by subsequent reoxidation.

A substantial amount of work will be accomplished on Tasks 1–4 during FY 2000. Task 5 will be completed in FY 2001–2002.

Research Progress

This report summarizes the research completed within the first seven months of this three-year project, mainly focused on Tasks 1, 3, and 4. In support of Task 1, at PNNL we have conducted several column experiments that involve treatment of Cr(VI)-contaminated soil samples with diluted H_2S. This includes large column tests conducted with an uncontaminated (background) soil sample from a waste site at White Sands Missile Range, New Mexico, where the first ISGR field test was conducted. The soil was treated with H_2S/N_2 or H_2S/air mixtures in two column tests, H_2S breakthrough data were collected, and the treated sediment was characterized. The results of these tests were used to develop a preliminary reactive transport model describing the interaction of H_2S, O_2, and the soil matrix. In particular, it appears that the soil iron oxides act as catalysts in the reaction between H_2S and oxygen in the H_2S/air test. Elemental sulfur was also identified as the predominant product of H_2S consumed during gas/soil interaction. Current testing activities are focused on soil samples obtained from the Hanford Site in, where a larger-scale field demonstration of the ISGR technology will be performed by DOE. Work-to-date on Hanford soil samples indicates that reduction of Cr(VI) to Cr(III) is essentially quantitative.

In order to understand the role of soil water chemistry for Cr(VI) reduction (Task 3), NMIMT is examining the reduction kinetics of Cr(VI) by H_2S in the aqueous phase. Analytical methods have been developed for chromate, sulfide, elemental sulfur, sulfite, thiosulfate, and sulfate. Cr(VI) reduction is being examined as a function of pH, Cr(VI) concentration, sulfide concentration, temperature, and ionic strength. In addition, manganese oxide and goethite were synthesized. These Fe- and Mn-oxides, as well as aluminum oxides and silica, will be used in the next stage to explore how various mineral surfaces affect Cr(VI) reduction in the aqueous suspensions.

Task 4 has been initiated by conducting a column reoxidation test with an H_2S-treated Hanford soil sample. This test involved pumping oxygenated water through the column until oxygen breakthrough was observed. This permitted calculation of the redox-buffering capacity of the treated soil. This value was found to agree with an estimate based on the ferrous content of the treated soil sample.

Planned Activities

Substantial progress is being made in FY 2000 that has greatly increased our understanding of reaction processes in the Cr(VI)-H_2S-O_2-soil system. In FY 2000–2001, we plan to continue with Tasks 1–4 to obtain information to support reactive transport modeling activities and design of ISGR field treatment systems.

- A substantial number of column tests will be performed on Hanford soil samples to define reaction stoichiometries and kinetics in the Cr(VI)-H_2S-O_2-soil system. This work includes performing tests over a range of gas flow conditions to obtain information on the rates of competing or coupled reactions. Treated soils are also being characterized for iron and sulfur products, and mass balance considerations will be employed to define the specific H_2S/soil reactions involved. Long-term oxidation tests (six-months duration) will also be performed on H_2S-treated soil samples to verify that the reduced chromium will not be reoxidized.

- Solid-gas phase interactions between synthesized iron oxides (e.g., ferrihydrite and hematite) and H_2S will be examined through column studies. The amount of H_2S consumed will be determined. The reaction products will be analyzed at PNNL by Mössbauer, x-ray photoelectron, and far-infrared spectroscopies. This will serve to better define H_2S interaction processes in soils.

- Experiments on aqueous phase Cr(VI) reduction by sulfide under various conditions will be completed and the reaction mechanism explored. In particular, the effect of oxygen will be tested.

- Potential catalysis of mineral surface on Cr(VI) reduction by sulfide will be examined using pure Fe-, Mn-, Al-, and Si- oxides as representative surfaces. Adsorption of both Cr(VI) and sulfide will be properly evaluated to understand the catalytic processes.

- Interactions between pure chromate compounds (e.g., K_2CrO_4, Na_2CrO_4, $BaCrO_4$, $CaCrO_4$) and H_2S gas will be tested. Reaction products will be analyzed at NMIMT by x-ray diffraction, scanning electron microscopy, and transmission electron microscopy with parallel electron energy-loss spectroscopy. In addition, testing activities will be extended in FY 2001 to include technetium and in FY 2002 to include uranium, thus potentially increasing the capabilities of the ISGR remediation approach.

Research results will be published in peer-reviewed publications. A website will also be created this summer to facilitate the information exchange among various interested parties.

Influence of Clastic Dikes on Vertical Migration of Contaminants in the Vadose Zone at Hanford

(Project Number: 70193)

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Specific DOE problem

This research project addresses the effect of clastic dikes on contaminant transport in the vadose zone. Clastic dikes are vertically oriented subsurface heterogeneities that are common at the Hanford Site, including the subsurface sediments below the tank farms in the 200 West Area. Previous studies have suggested that clastic dikes may provide a fast path for transport of leaking fluid from the tanks through the vadose zone.

Research Objectives

This research will test the hypothesis that clastic dikes at the Hanford Site provide preferential pathways that enhance the vertical movement of moisture and contaminants through the vadose zone. Current flow and transport models of the vadose zone at the 200 Areas are based on relatively simple hydrogeologic models that assume horizontally layered sediments with no preferential vertical flow paths. To address those scientific needs, our proposed research includes field and modeling studies of the spatial distribution of clastic dikes, the hydrologic properties within dikes, and the potential effect of clastic injection dikes on fluid flow through the vadose zone. The data and models of the clastic dike networks produced for this project should be directly applicable to fate and transport studies conducted at the 200 West Hanford tank farms.

Research Progress and Implications

This report summarizes progress after the first eight months of a three-year project. The major accomplishment thus far has been mapping the spatial distribution of clastic dikes over an area of about 60 square kilometers using aerial imagery and a geographic information system (GIS). The mapping was performed over an area of the Hanford Site south of the tank farms where cultural features and sand dunes are not present and thus do not obscure the pattern of the dikes. Analysis of the map data thus far includes statistical analysis of the length and orientation of the clastic dikes. The mapping and analysis have revealed several important properties of the clastic dike network at the site. The most important is the apparent presence of trends in size. These trends were used to guide the placement of transects where detailed data were recorded in the field. Geologic measurements were made along the transects to confirm the location of the dikes estimated from the aerial imagery and to estimate the thickness of the clastic dikes intersecting the transects. Geophysical field work to map the distribution of clastic dikes, a detailed ground-penetrating radar (GPR) survey (observations spaced 10 cm apart) on the longest transect, approximately 7 km long, was recently completed. The GPR survey was successful and will provide an independent estimate of the spacing and thickness of the clastic dikes on the transect. In addition to the transect, two 2-D GPR surveys (2-m spacing between lines, 10-cm spacing along lines) were recorded at locations that are being examined as possible sites for performing characterization and infiltration experiments. These experiments, which are described below, will be performed in August 2000. The GPR data will be used to map the dikes in the proposed test areas. Processing of the GPR data is underway.

Planned Activities

Additional fieldwork will be conducted at the Hanford Site in July and August of 2000. This will include application of advanced characterization methods, air-mini-permeametry and infrared (IR) imaging to examine the distribution of hydrogeological properties within clastic dikes that have been exposed by excavations. Preliminary infiltration experiments will also be performed at the field sites to gather data for planning purposes. Data from the fieldwork will be analyzed during the last quarter of FY 2000 and the first quarter of FY 2001 using geostatistical methods. In tandem with that analysis, fieldwork will be planned for spring 2001 that will include a field-scale infiltration experiment over a clastic dike. The experimental site will be characterized and monitored during the infiltration experiment using advanced geophysical methods such as GPR, time domain reflectometry, and electrical resistance tomography. Geostatistical methods will be used in FY 2001–2002 to provide numerical 3-D grids of the infiltration site for flow and transport modeling, and the resulting transport models will then be compared with the actual observations during the transport experiments.

Quantifying Vadose Zone Flow and Transport Uncertainties Using a Unified, Hierarchical Approach

(Project No: 70187)

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Research Objectives

This project recognizes the difficulties in predicting field-scale vadose zone transport raised by the small-scale variability of vadose zone flow and transport properties and the large scale of the typical contamination problems facing DOE. We are developing and demonstrating a general approach to parameterize models of flow and transport in the heterogeneous vadose zone that is practical at the field scale. Scientific goals include investigating the application of recent advances in indirect measurement of soil properties to the conditional simulation of flow and transport in the heterogeneous vadose zone; determining the relationships between the type of data used in the conditional simulation, the quantity of data available, the scale of measurement, and the uncertainty in predictions of flow and transport; and developing guidance for the effective application of the model parameterization and conditional simulation approach at field scales common to DOE vadose zone contamination problems.

This investigation is being conducted using data from large-scale, controlled field experiments conducted on the Hanford Site. Because the scale of these experiments is comparable to that of DOE's contamination problems, we will be able to elucidate relationships between the quantity and spatial extent of characterization data and the accuracy and uncertainty of flow and transport predictions. We envision that this research will demonstrate a systematic approach for cost-effectively parameterizing spatially variable models of the vadose zone and that the results will provide guidance for allocating vadose zone characterization resources.

Research Progress and Implications

This report summarizes work after five months of a three-year project. The project is developing and demonstrating a vadose zone parameterization method using data from a field experiment conducted in 1980–81 in the 200 East area of the Hanford Site (the Sisson and Lu Site). Additional data from this site were collected in 1995 using detailed geophysical borehole logging. As part of the Hanford Site Science and Technology Program, an additional infiltration/tracer experiment is being planned for the Sisson and Lu Site. This experiment will be conducted during the spring/summer of this year (2000) and will include advanced geophysical measurements (such as electrical resistivity tomography and cross-borehole ground-penetrating radar) as well as more conventional measurements of soil moisture and matrix potential and tracer concentrations. This project staff has been collaborating with the Hanford Science and Technology Program in planning for this additional experiment. This has involved attendance at planning workshops and review of the test plan. Relevant data and the results of analyses will be shared freely between project staff and that of the Hanford program. All data from the Sisson and Lu Site will be used in the analyses conducted under this project. The primary work under this project will be conducted after the Hanford experiment has been conducted and additional data needed for our analyses (soil hydraulic property measurements at the Sisson and Lu Site) have been collected.

This project is using pedotransfer functions derived from neural network analyses to determine the utility of such indirect measurements in large-scale predictions and to examine the effect on uncertainty in transport predictions from using indirect measures of soil hydraulic properties. To develop the pedotransfer functions, we have assembled the relevant unsaturated hydraulic property data from the Hanford Site and are analyzing these data.

Planned Activities

Core samples will be obtained from the Sisson and Lu Site upon completion of the Hanford Science and Technology Program experiment. This activity is scheduled for the latter half of June 2000. Samples will be analyzed at the U.S. Salinity Lab for water retention, unsaturated hydraulic conductivity, and physical properties. Sample analysis is anticipated to take approximately two months. The hydraulic properties are required for the scaling analysis used in the parameterization/conditional simulation approach. Data analysis will be conducted in collaboration with the Hanford Site researchers. Scaling and geostatistical analyses using the newly obtained hydraulic data will be conducted by this project staff. These analyses will be initiated in August or September 2000. The neural network analyses using the currently available Hanford Site data will continue. The additional data will be included in the analysis when they become available. The simulation activities to be conducted under this project will begin in FY 2001.

Radionuclide Sensors for Water Monitoring

(Project Number: 70179)

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Research Objective

Radionuclide contamination in the soil and groundwater at Department of Energy (DOE) sites is a severe problem requiring monitoring and remediation. Radionuclide measurement techniques are needed to monitor surface waters, groundwater, and process waters. Typically, water samples are collected and transported to the analytical laboratory, where costly radiochemical analyses are performed. To date, there has been very little development of selective radionuclide sensors for alpha- and beta-emitting radionuclides such as ^{90}Sr, ^{99}Tc, and various actinides of interest.

The objective of this program is to investigate novel sensor concepts and materials for sensitive and selective determination of beta- and alpha-emitting radionuclide contaminants in water. To meet the requirements for low-level, isotope-specific detection, the proposed sensors are based on radiometric detection. As a means to address the fundamental challenge of short ranges of beta and alpha particles in water, our overall approach is based on localization of preconcentration/separation chemistries directly on or within the active area of a radioactivity detector, using automated microfluidics for sample manipulation and sensor regeneration or renewal.

The outcome of these investigations will be the knowledge necessary to choose appropriate chemistries for selective preconcentration of radionuclides from environmental samples, new materials that combine chemical selectivity with scintillating properties, new preconcentrating column sensors, and improved instrumentation and signal processing for selective radionuclide sensors. New knowledge will provide the basis for designing effective probes and instrumentation for field analytical chemistry.

Research Progress

This report summarizes work performed in the first six months of a three-year program. The initial ongoing effort is directed at the investigation of the preconcentration column sensor concepts, development and characterization of the selective scintillating microspheres (SSMs), and development of the new scintillation detection systems. The preconcentrating minicolumn radionuclide sensor is based on the use of dual-functionality bead materials. These materials are designed to incorporate both selective separation chemistry for analyte preconcentration and localization within the detector, and scintillating fluors, so that radioactivity of retained species can be transduced to a measurable light output. To date we have achieved progress in SSM materials prepared by co-immobilization of selective organic extractants and scintillating fluors within inert polymeric beads. Scintillating microspheres selective for technetium, strontium, and actinides were prepared. Using pertechnetate-selective scintillating beads, we have demonstrated the feasibility of a renewable preconcentrating column sensor concept in successful application toward ^{99}Tc determination in contaminated ground water samples from the Hanford Site. To avoid sensor material degradation during the regeneration step, the sensor column was renewed via fluidic bead replacement. Using a 50-mL sample volume and 30-minute counting time, the detection limit for ^{99}Tc was 0.37 dpm/mL (9.8 pg/mL). This detection limit is below the maximum permissible drinking water level of 2 dpm/mL. This study is a subject of a recent publication (1).

In addition, research has begun on a combined extraction chromatographic and scintillation resin in a solid support for on-line and off-line monitoring of radiostrontium in aqueous solutions. This extractive scintillator resin has been realized as 1) a mixture of extraction chromatographic resin and granular scintillator, 2) extraction chromatographic material coated on the surface of a scintillating glass and 3) inert polystyrene chromatographic resin impregnated with a proprietary extractant and organic fluors. The extractive scintillator resin has been evaluated for on-line and off-line applications. For on-line measurements, the extractive scintillator resin is used in conjunction with a flow-cell scintillation detection system. For off-line measurements, the resin is used in the same manner as the non-scintillating version, but rather than eluting the activity from the column prior to counting, the scintillating extraction column can be placed in a scintillation vial and counted without the introduction of liquid scintillation cocktail. The absolute detection efficiency for ^{90}Sr beta particles sorbed to the strontium-selective extractive scintillator resin was measured to be approximately 30%. Characterization of the detection efficiency, minimum detectable concentration, selectivity, loading capacity, capacity factor and regeneration capability of the extractive scintillator resin continues.

Actinide SSMs have been developed and characterized to determine feasibility for sequential elution of radioactive species. Tests have indicated that although sequential separation is feasible, available energy resolution information is limited. In addition to the limited energy resolution of the SSM, variable quench associated with different chemical eluants is significant. The absolute detection efficiency of the actinide SSM depends on alpha energy and ranges from ~80% to nearly 100% (2).

Planned Activities

Within the remainder of the first year and during the second year, our activities will be directed at further developing SSM materials for ^{90}Sr and actinide sensing. We will explore SSM materials and sensor concepts based on selective ligands covalently attached to the bead support. Inorganic sorbent and scintillating materials will be evaluated for use with the preconcentrating column sensors. We plan to evaluate the feasibility of selective scintillating sensor concepts in fiber and planar geometries.

Information Access

DeVol TA, JE Roane, JM Williamson, JM Duffey, and JT Harvey. 2000 "Development of scintillating extraction media for separation and measurement of charged-particle emitting radionuclides in aqueous solutions." *Radioactivity and Radiochemistry* (submitted).

DeVol TA, OB Egorov, JE Roane, A Paulenova, and JW Grate. April 2000. "Extractive scintillating microspheres for ^{99}Tc quantification in aqueous solutions." Fifth International Conference on Methods and Application of Radioanalytical Chemistry, Kailua-Kona, Hawaii.

Duffey JM, A Paulenova, and TA DeVol. April 2000. "Combined extraction chromatography and scintillation detection for on-line and off-line monitoring of strontium in aqueous solutions." Fifth International Conference on Methods and Application of Radioanalytical Chemistry, Kailua-Kona, Hawaii.

Egorov OB, SK Fiskum, MJ O'Hara, and JW Grate. 1999. "Radionuclide sensors based on chemically selective scintillating microspheres: Renewable column sensor for analysis of ^{99}Tc in water." *Anal. Chem*. 71:5420-5429.

Integrated Field, Laboratory, and Modeling Studies to Determine the Effects of Linked Microbial and Physical Spatial Heterogeneity on Engineered Vadose Zone Bioremediation

(Project Number: 70165)

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Problem Addressed

The specific DOE problems being addressed are the large inventories of contaminants in deep vadose zones in the semiarid western U.S. and the ongoing contamination of the saturated zone by contaminants migrating through these deep vadose zones. In situ bioremediation of contaminants can offer advantages over physical removal methods in cost, speed, public acceptance, and final cleanup levels achieved. However, there are uncertainties about the feasibility of bioremediation of recalcitrant contaminants in deep vadose zones where microbial populations are low and discontinuous, and about how hydrologic features of the vadose zone control microbiological processes. These uncertainties call into question the accuracy of predictions in vadose zone flow and transport models.

Research Objective

The overall objective of this research is to provide DOE with an increased understanding of the effect of interacting hydrologic and microbiological processes that control the feasibility of engineered bioremediation of chlorinated compounds in heterogeneous, microbially sparse, deep vadose zones. The specific project objectives are to

1. determine the occurrence and distribution of denitrifiers and methanotrophs in the deep vadose zone at the Hanford Site

2. determine bioreactor kinetics for carbon tetrachloride removal in the presence of methane, nitrous oxide, and triethyl phosphate by denitrifiers (carbon tetrachloride to chloroform) and methanotrophs (chloroform to carbon dioxide) isolated from the field site

3. determine the rate and extent of microbial colonization in response to gas-phase nutrient injection

4. use this information to develop an improved vadose zone reactive transport model and explore the level of site heterogeneity information that is needed for accurate premodeling of attenuation of vadose zone contaminant transport by engineered bioremediation.

Research Progress

This report summarizes work after six months of a three-year project. Field samples are required to address the first two specific objectives. Due to cost considerations, we must obtain samples from coring activities being conducted by other programs. We are working with DOE-RL to identify opportunities to obtain vadose zone samples near and within the carbon tetrachloride-contaminated zone at the Hanford Site. The best near-term opportunity appears to be with the Innovative Treatment Remediation Demonstration (ITRD) program.

In recent discussions with DOE-RL, we discovered that injection of non-engineered microorganisms and aqueous-based nutrient delivery are potentially acceptable technologies at DOE sites. With this information and due to the delay in obtaining field samples, we have decided to pursue the third specific objective using *Pseudomonas stutzeri* strain KC rather than isolates from the field site. Strain KC is capable of high rates of degradation and is the only known bacterium able to degrade carbon tetrachloride without producing chloroform. Studies are being planned to examine the ability of strain KC to colonize sediment (from a single inoculation point) as a function of varying 1) water-filled porosity, 2) pore throat size, 3) aqueous nutrient concentration, and 4) distance from a nutrient injection point.

The STOMP code (http://www.pnl.gov/etd/stomp) is the most highly developed vadose zone flow and transport model but does not include biological processes. Building on previous National Science Foundation funding to Dr. Selker, this project is modifying the STOMP code to include microbial reaction rate source/sink terms and cell attachment/detachment terms (specific objective 4). Experimental work on validation of these new components of STOMP is ongoing. This research will provide DOE with a vadose zone flow and transport code that incorporates biological processes and couples hydrologic and biologic processes.

Planned Activities

- Continue to work with DOE to identify sampling opportunities and obtain pertinent field samples to accomplish the first two specific objectives.

- Examine the ability of strain KC to colonize vadose zone sediment (from a single inoculation point) as a function of varying water-filled porosity, pore throat size, aqueous nutrient concentration, and distance from a nutrient injection point (FY 2000). Studies will be extended in FY 2001 to examine colonization as a function of important vadose zone hydrological processes such as funnel flow along inclined textural interfaces.

- Use the above experimental results to further develop and validate the biological component of STOMP.

Health Effects

Linking Molecular Events to Cellular Responses at Low Dose Exposures

(Project Number: 69941)

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Research Objective

The studies proposed in this project are to define thresholds in cell signaling pathways that are required for cellular transformation and may be targeted by low-dose radiation. Defining thresholds in transformation-related signal transduction pathways that are sensitive to low-dose radiation would be an important advancement in risk assessment and could be used to demonstrate nonlinear relationships between low-dose radiation and cancer.

Research Progress

This report summarizes work after five months of a three-year project. Efforts are under way to develop the molecular tools required to investigate thresholds in transformation-related signal transduction pathways. Dose response for a polypeptide tumor promoter (epidermal growth factor [EGF]) has been conducted in a 12-O-tetradecanoyl phorbol-13-acetate (TPA) responsive element (TRE)-luciferase reporter cell line to establish the linear range of the TRE-reporter assay for extension to low-dose radiation studies. Exposure conditions for examining dose-rate effects on the transformation response to EGF have been investigated and the exposure system modified to minimize priming effects due to sham exposure.

New stable transfectant JB6 reporter cell lines have been generated. These are to serve as readouts for measuring induced Erk activation or activation of transcription factors AP-1 or NF-κB. Thus far, 4X AP-1-luciferase/JB6 Cl 41 P+ cells and 5X NF-κB-luciferase Cl 41 reporter cells have been generated and drug selected. Multiple clones are about to be screened for low basal activity and greater than two-fold inducibility by TPA. Four reporter clones will be chosen for each transcription factor.

Another readout for activation of Erk is activation of the fusion substrate Gal4-Elk. We have experimental evidence that inhibition of the Erk kinase MEK by U01267 inhibits Erk-dependent Gal4-Elk activation in a dose-dependent fashion. We expect to obtain parallel measurement of phosphoErk levels for each concentration of MEK inhibitor, thus permitting a direct correlation of Elk activation level with concentration of activated (phosphorylated) Erk. Note that Gal4-Fra-1 activation is also dependent on Erk activity. This exciting discovery is the subject of a manuscript soon to be submitted. Transient transfection of SRE-luciferase also demonstrates quantitative dependency on activated Erk levels. Finally AP-1-luciferase reporter activation (transient transfection) is concentration dependently regulated by activated Erk levels. Measurements of superoxide dismutase activity have been optimized using an enzyme-linked immunosorbent assay (ELISA).

Planned Activities

The construction of a tetracycline-inducible dominant negative Erk construct is under way. We have generated JB6 P+ cells that harbor the tetracycline regulator (G418 selection). Once the TRE-DNErk is available it will be transfected into the tet regulator cells (hygromycin selection). These inducible DNErk cells will allow us to regulate the cellular concentration of activated Erk precisely.

Superoxide dismutase activity will be determined in vivo and in vitro following exposure to low-dose gamma radiation. Changes in SOD activity will be confirmed at the protein level by Western blot for specific SOD activities.

Yet to be generated: SRE-luciferase/P+ cells. These will provide quantitative readout for Erk activation. Following full optimization of the radiation exposure system, the effect of dose and dose-rate on transformation by EGF and TPA will be determined.

Information Access

As mentioned above, the work describing the Erk dependent Gal4-Elk activation is being prepared for publication.

Sensitivity to Radiation-Induced Cancer in Hemochromatosis

(Project Number: 69939)

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Research Objectives

The objectives of this pilot project using HFE-knockout homozygotes and heterozygotes are to 1) determine whether the knock-out mice have greater sensitivity to radiation-induced cancer of the colon, liver and breast, 2) establish the dependence of this sensitivity on the accumulation of iron, 3) determine the extent to which cell replication and apoptosis occur in these target tissues with varying iron load, and 4) correlate the increases in sensitivity with changes in insulin-related signaling in tumors and normal tissue from each target organ.

Three experimental designs will be used in the pilot project. The sequence of experiments is designed to first explore the influence of iron load on the response and demonstrate that HFE knockout mice are more sensitive than the wild type to radiation-induced cancer in one or more of three target tissues (liver, colon and breast). The dose response relationships with a broader set of radiation doses will be explored in the second experiment. The final experiment is designed to explore the extent to which heterozygotes display the increased susceptibility to cancer induction and to independently assess the importance of iron load to the initiation versus promotion of tumors.

Research Progress and Implications

Breeding pairs of HFE knockout mice were obtained for establishing a breeding colony in our laboratory. A colony has now been established with sufficient numbers of mice to support the experimental design of this project. In addition, wild-type mice (C57BL/6J) have been obtained to serve as controls for the studies. For the first experiment, 30 HFE knockout and 30 wild-type breeding pairs were started on a low-iron diet (30 mg/kg) on the first day of mating. Offspring from these matings have become the first experiment. Groups of 20 mice (bred and raised on the low-iron diet) will be fed purified iron diets as follows: 30, 300, 3000 mg/kg iron for the HFE mice and 30, 300, 3000, and 20,000 mg/kg iron for the C57BL/6J wild-type mice. These mice will be irradiated (1 Gy colbalt-60) at about 30 days of age. Two additional groups of nonirradiated mice (one HFE and one wild-type) will be fed the 30 mg/kg diet and used as controls.

Planned Activities

If this pilot project is successful in demonstrating substantive differences in sensitivity in one or more of these organs, a larger effort will be proposed to focus on low-dose and dose-rate effects of radiation with the intent of identifying nonlinearity and/or thresholds in the dose-response relationships. This follow-on study would concentrate on understanding the molecular basis of interactions between Hereditary Hemochromatosis and radiation exposure. The additional work would allow us to calculate the excess risk that would be associated with low doses of radiation in the human population under EPA’s draft Cancer Risk Assessment Guidelines. More important, it should provide tools that can be applied to studying this relatively large segment of the population that could have enhanced sensitivity to radiation with a focused effort in molecular epidemiology.

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