High-Level Waste

Electroactive Materials for Anion Separation - Technetium from Nitrate

Project ID: 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 ethylene-diamine 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 de-ionized water, the much-reduced capacity of ABEC 5000 resins in comparison to 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.

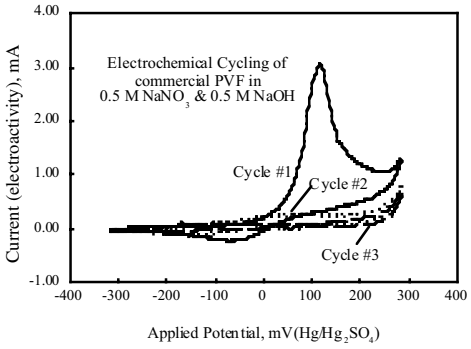
Alternative IX materials that have high capacities, can be regenerated easily, and are highly selective for TcO_4^- would avoid these problems. Electrochemically active IX media meet these criteria. Such an IX system uses electrically induced changes in the media to expel sorbed ions through a charge 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.

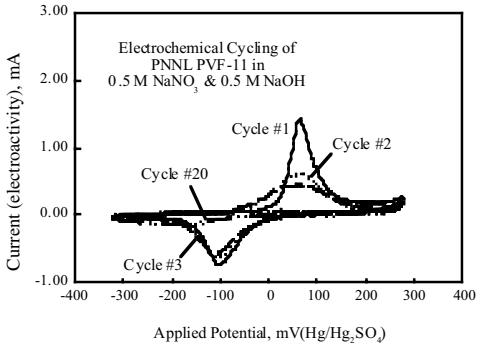
The focus of the project is to develop a fundamental understanding of how the physical and chemical properties of electroactive ion exchange (EaIX) materials control their efficiency when used as mass separation agents. Specifically, the desirable characteristics of EaIX materials for separation applications 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 share 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 3-year project. The two components of the project are (1) synthesis and (2) characterization of EaIX materials. The monomer constituents of the electroactive polymer ultimately control the desirable characteristics described earlier. We have, therefore, focussed our efforts in the synthesis monomers with the appropriate functional groups. From our discussions with the Tank Focus Area's Technology Integration Manager for Pretreatment, Phil McGinnis, 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). The figure below compares the characteristics of PNNL-synthesized and commercially available PVF polymers; the commercial PVF is deactivated in less than 2 cycles. Although PNNL PVF-11 is mainly deactivated after 20 cycles, our study where we are systematically modifying the basic ferrocene units to make the resulting polymer more stable in alkaline conditions is not completed, and therefore, we are very 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 listed earlier (mainly #3 and #4). Initial attempts of using phase-inversion techniques with commercial PVF for making high-capacity electrodes (#5 above) 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. Most of the problems in collecting spectra at the Fe K edge accrue from the large background from the ReO_4^- ions, which 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 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 done on ferrocenium perrhenate, dimethylferrocenium perrhenate and ferrocenium nitrate, that 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. Recently obtained XAS results mentioned above are currently being analyzed.

Information Access

Hubler, T.L., G.M. Anderson, J.H. Sukamto, M.A. Lilga, and S.D. Rassat. "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, August 22-26, 1999, New Orleans.

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Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation

Project ID: 59982

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Research Objectives

This project provides information relevant to: (i) extent and nature of radiation-induced chemical modification of Hanford waste during storage and (ii) potential applications of peroxynitrite in remediation technologies.

Specific objectives are 1. To determine the extent of radiation-induced peroxynitrite generation in mixtures simulating the various phases of nuclear waste. 2. Through mechanistic studies of catalyzed peroxynitrite reactions to estimate their contribution to the degradation of organic waste components and to determine the feasibility of using peroxynitrite for the destruction of organic complexants and for the removal of chromium for more efficient vitrification.

Research Progress and Implications

This report summarizes work after 2.5 years of a 3 year project. Peroxynitrite, $ONOO^-$, is a powerful oxidant when protonated or combined with CO_2 or metal ions. These reactivity pathways have been investigated, starting with the catalyzed decomposition reactions. Mechanistic studies has demonstrated that ONOOH undergoes homolysis producing the strongly oxidizing $^{\bullet}NO_2$ and $^{\bullet}OH$ radicals with a 28% yield. An extensive oxidation of EDTA was found in the presence of excess of ONOOH. Similarly, CO_2-catalyzed oxidations by peroxynitrite proceeds via formation of the $^{\bullet}NO_2$ and $^{\bullet}CO_3^-$ radicals with a 35% yield. The carbonate radical has shown to be a strong acid, contrary to the previous reports of low radical acidity. The pulse radiolysis studies have shown that both $^{\bullet}OH$ and $^{\bullet}CO_3^-$ rapidly oxidize $ONOO^-$, generating an unstable $^{\bullet}ONOO$ radical, which decomposes into $^{\bullet}NO$ and O_2. Collectively, these studies have clarified all significant issues concerning the H^+- and CO_2-catalyzed reactivities of peroxynitrite. It is concluded that $ONOO^-$ can be an important source of oxygen within Hanford waste and may contribute to the generation of $^{\bullet}NO$ and N_2O emitted from the storage tanks. Reactive radicals produced in the H^+- and CO_2-catalyzed peroxynitrite reactions can contribute to the chemical modification of the waste during its storage.

Oxidation of Cr(III) by peroxynitrite has been investigated in concentrated alkaline solutions. This reaction cleanly produces Cr(VI) in the form of highly soluble chromate, with the stoichiometric ratio $\Delta[ONOO^-]/\Delta[Cr(III)] = 3/2$, indicating that the oxidation equivalent of $ONOO^-$ is utilized completely. The rate-determining step of this reaction is an S_{N2} nucleophilic attack of $ONOO^-$ on $Cr(OH)_4^-$, for which a rate constants of 6.5 $M^{-1}s^{-1}$ has been determined. Comparative studies showed that peroxynitrite is significantly better oxidant for Cr(III) than hydrogen peroxide, frequently used for this purpose. Above the solubility limit of Cr(III), the oxidation rate depends upon the solution aging due to formation of polymeric species; the hydrolysis of the polymer becomes the rate-limiting step under these conditions. The oxidation of Cr(III) is strongly promoted by the presence of Mn(II), which not only accelerates the reaction, but also virtually eliminates the effects of aging. Several transition metals have been tested as catalysts for EDTA oxidation in alkali. Remarkably, even in the absence of a catalyst, EDTA was degraded simultaneously with the decay of $ONOO^-$ during 5-10 hours. Copper(II)-based catalysts (CuEDTA and Cu on SiO_2) were the most active causing -80% oxidation within one hour. Thus, applications of peroxynitrite for the destruction of the waste organics and for the oxidative removal of chromium appear to be promising.

Both UV- and γ-radiation generate $ONOO^-$ in solid nitrates, as shown by the optical and Raman spectral changes and the chemical analyses upon dissolution. Similarities between photolysis and radiolysis suggest that $ONOO^-$ is produced via isomerization of an electronically excited NO_3^- ion. Although the initial radiation yields of $ONOO^-$ are significant (-1 molecule per 100 eV of absorbed energy), the accumulation decelerates with time reaching a steady-state level due to competing radiolytic decomposition of $ONOO^-$; the data indicate that a long-range electron transfer and an unusual radical chain reaction are involved in the decomposition process. γ-radiolysis of concentrated nitrate solutions, also generates $ONOO^-$ via both direct radiation absorption by NO_3^- and an indirect pathway. The main conclusion from these studies is that the radiation-induced generation of peroxynitrite is an efficient process in both solid nitrates and their concentrated solutions, which can contribute very significantly to the chemistry of Hanford wastes.

Planned Activities

Mechanistic time-resolved studies of radiation-induced peroxynitrite generation and decomposition in solid nitrates. Development of protocols for oxidative destruction of complexants and dissolution of chromium.

Publications

Lymar S.V., Hurst J.K., "CO_2-catalyzed One-Electron Oxidations by Peroxynitrite: Properties of the Reactive Intermediate", *Inorg. Chem.*, ***37***, 294-301 (1998)

Goldstein S., Saha A., Lymar S.V., Czapski G., "Oxidation of Peroxynitrite by Inorganic Radicals: A Pulse Radiolysis Study", *J. Am. Chem. Soc.*, ***120***, 5549-5554 (1998)

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Gerasimov O. V., Lymar S. V., "Pathways of Decomposition and One-Electron Oxidation by Peroxynitrous Acid", *Nitric Oxide*, ***3***, 7, (1999)

Czapski G., Lymar S.V., Schwarz H.A., "Acidity of the Carbonate Radical", *J. Phys. Chem. A*, ***103***, 3447-3450 (1999)

Lymar S.V., Schwarz H.A., Czapski G., "Medium Effects on Reactions of the Carbonate Radical with Thiocyanate, Iodide, and Ferrocyanide", *Radiat. Phys. Chem.*, in press

Gerasimov O. V., Lymar S. V., "Oxidation of Chromium(III) by Peroxynitrite in Alkaline Solutions", *Environ. Sci. Technol.*, submitted

Coddington J.W., Wherland S., Hurst J.K., "Pressure Dependence of Peroxynitrite Reactions. Support for a Radical Mechanism", *Inorg. Chem.*, submitted

Lymar S. V., Yurchenko E. N., Wishart J. F., Gerasimov O. V., "Radiation-Induced Formation and Decay of Peroxynitrite in Solid Alkali Nitrates", *J. Phys. Chem.*, submitted

Design and Synthesis of the Next Generation of Crown Ethers for Waste Separations: An Inter-Laboratory Comprehensive Proposal

Project ID: 55087

Dr. Bruce A. Moyer, Oak Ridge National Laboratory

Research Objectives

A combined effort at Oak Ridge, Pacific Northwest, and Argonne National Laboratories and the University of Tennessee is proposed to design, synthesize, and characterize the next generation of crown ethers for metal-ion separations applicable to USDOE's environmental needs. This research combines three inter-dependent projects dealing with 1) molecular mechanics and ligand design, 2) solvent-extraction properties, and 3) resin-immobilized crowns. Despite impressive developments in the chemistry of crown ethers, factors such as the need for polar environments and "forcing" conditions, weak efficiency, and dependence on matrix anions limits their potential in separations. Exploiting advances in molecular mechanics, this research seeks accelerated progress through ligand design and synthesis coupled with testing of predictions via structural, spectroscopic, and separation techniques. New crown compounds will be studied in solvent-extraction and polymer systems, emphasizing ion-exchange features. Selectivity principles governing the binding of such ions as Li^+, Cs^+, Sr^{2+}, and Ra^{2+}, all of which have been identified as contaminants at USDOE sites, will be investigated. The partner laboratories have world-recognized programs in the area of crown ethers, solvent extraction, and ion exchange. Their cooperation under this research represents an unusual and extremely effective combination of unique resources.

Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation and Recycle of Sodium Hydroxide and Sodium Nitrate

Project ID: 65339

Bruce A. Moyer, Oak Ridge National Laboratory

Prof. Alan P. Marchand, University of North Texas

Research Objective

The major objective of this research is to explore new liquid-liquid extraction approaches to the selective separation of sodium hydroxide from alkaline high-level wastes stored in underground tanks at the Hanford and Savannah River sites. Secondary priority is given to separating potassium and abundant anions, including nitrate, nitrite, aluminate, and carbonate. Salts of these ions represent possible additional value for recycle, alternative disposal, or even use as commodity chemicals.

A comprehensive approach toward understanding the extractive chemistry of these salts is envisioned, involving systems of varying complexity, from use of simple solvents to new bifunctional host molecules for ion-pair recognition. These extractants will ideally require no adjustment of the waste composition and will release the extracted salt into water, thereby consuming no additional chemicals and producing no additional waste volume. The overall goal of this research is to provide a scientific foundation upon which the feasibility of new liquid-liquid extraction chemistry applicable to the bulk reduction of the volume of tank waste can be evaluated.

Research Progress and Implications

This report summarizes work performed during the first eighteen months of a three-year project. Initial experiments have focused on identifying candidate extraction systems possessing appreciable loading, effective stripping with water, and adequate selectivity for hydroxide. An exciting new class of readily available and potentially economical extractants has been identified and tested in a water-immiscible process-suitable diluent. The actual composition of the solvent is presently proprietary and is consequently not disclosed in this report. A patent application has been filed as a first step toward attracting users and ultimately transferring the technology. Selective extraction of sodium hydroxide was demonstrated in several systems involving simple aqueous phases and complex waste simulants. Quantitative recovery of sodium hydroxide by stripping with water was demonstrated, and it was shown that certain solvents could be cycled several times without loss of performance. Selectivity for hydroxide over nitrate transfer exceeds 20:1. Caustic recycle applications include recycle of sodium hydroxide at several DOE sites as well as in certain industrial processes.

Synthesis of novel cage-functionalized crown ethers and podands is being carried out by Prof. Alan Marchand and his group at the University of North Texas (UNT). These cation receptors offer the potential to enhance sodium hydroxide separation efficiency and selectivity, and indeed this has been shown to be the case among several nitrogen-containing macrocycles that have been prepared and tested. These successful initial investigations have provided valuable information that is guiding continuing efforts to design more effective host species.

Planned Activities

During the remainder of the project, we plan to probe the properties and underlying chemistry of the selective separation of NaOH from aqueous mixtures using the compound classes identified in the

past eighteen months. Toward attracting the interest of the EM Tanks Focus Area and potential users, experiments are being conducted to boost the extraction efficiency so that 90% of the sodium hydroxide can be removed from the tank waste. Recent results show promise at higher temperatures, where it is possible to operate with up to 1 M extractant and where precipitation of aluminum hydroxide can be avoided. However, the results point to the need to increase the organic-phase solubility of the extraction complexes, either through synthesis of more soluble extractant derivatives or through use of alternative diluents. It is hoped that the 90% separation goal can be reached by the conclusion of the fiscal year. In FY 2001, work will focus on gaining a firmer understanding of candidate systems and exploring other properties, such as stability, needed for development of a robust process. Synthesis of both simple compounds and macrocycles will be continued, and these efforts will be guided both by results of crystal structures that provide detailed information on conformation and coordination and by extraction experiments that illuminate extraction behavior and thermodynamics..

Information Access and Selected Publications

See www home page of the ORNL Chemical Separations Group: http://www.ornl.gov/csg

B. A. Moyer, C. K. Chambliss, P. V. Bonnesen, and T. J. Keever, "Solvent and Process for Recovery of Hydroxide from Aqueous Mixtures," Patent Application Ser. No. 09/404,104, Sept. 23, 1999.

B. A. Moyer, P. V. Bonnesen, C. K. Chambliss, T. J. Haverlock, A. P. Marchand, H-S. Chong, A. S. McKim, K. Krishnudu, K. S. Ravikumar, V. S. Kumar, and M. Takhi, "Use of Cage-Functionalized Macrocycles and Fluorinated Alcohols in the Liquid-Liquid Extraction of NaOH and other Sodium Salts," ACS Symposium Series, American Chemical Society, Washington, DC (Submitted).

A. P. Marchand, and H.-S. Chong, "Synthesis and Alkali Metal Picrate Extraction Capabilities of Novel, Cage-Functionalized Diaza(17-crown-5) Ethers", *Tetrahedron* **1999**, *55*, 9697-9706.

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

Project ID: 65368

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Linfeng Rao, Lawrence Berkeley National Laboratory
Sue B. Clark, Washington State University
Nancy J. Hess, Pacific Northwest National Laboratory

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 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, current sludge washing processes are not effective in removing Cr. 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 including the complex chemistry of Cr, lack of fundamental data applicable to the HLW chemical systems (high heterogeneity, high ionic strength, high alkalinity and the presence of inorganic and organic ligands, etc.), and the need to avoid processes that may adversely enhance the solubility of Pu 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 Berkley 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 3-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. Specifically, studies were conducted to 1) to measure the solubility of $Cr(OH)_3$(am) in NaOH and in mixed solutions containing NaOH and $NaNO_3$,and 2) determine oxidation of Cr(III) to Cr(VI) by H_2O_2 in alkaline solutions.

The $Cr(OH)_3$(am) was prepared according to the method described by Rai et al. (1987) and was suspended in NaOH ranging in concentration from 0.01 to 10 M. The observed Cr concentrations in solutions filtered through 0.2µm and 0.0018µm 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 XAS showed that Cr(III) is the dominant oxidation state in the aqueous and solid phases. The solubility of $Cr(OH)_3$(am) were 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 Cr concentrations were observed with the increase in $NaNO_3$ concentrations from 0.1 to 6.0 M. As observed with solubility in NaOH, gradual decrease in solubility with the increase in equilibration period were observed.

Thermodynamic interpretations of these data will be done 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 successfully used to separate monomeric, dimeric, and trimeric Cr(III) species from the "bulk" Cr(III) solution. The separated species have been characterized by UV/Vis absorption spectroscopy. Kinetic experiments indicate that the three Cr(III) species with lower degrees of oligomerization (monomer, dimer, trimer) are easily oxidized by hydrogen peroxide in alkaline solutions as compared with the "bulk" Cr(III). The oxidation of the monomer, dimer, and trimer followed a first-order reaction order 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 1) solubility of $Cr(OH)_3$(am) in different electrolytes will be continued and will be used to develop a thermodynamic model to predict Cr(III) behavior in tank solutions, 2) kinetics of oxidation of Cr(III) to Cr(VI) in the presence of different oxidants and at room and elevated temperatures will be continued to provide fundamental data for effective oxidants, relevant to tank solutions, to oxidize Cr(III) to Cr(VI).

Chemical Speciation of Inorganic Compounds Under Hydrothermal Conditions

Project ID: 60050

Edward A. Stern, University of Washington

John L. Fulton, Pacific Northwest National Laboratory
Gerald Seidler, University of Washington

Research Objective

This project utilizes the high-intensity x-rays available at the Advance Photon Source (APS) to study the inorganic chemistry associated with tank waste vitrification. Although the chemical conversion of waste under high-temperature conditions is an integral part of these processing technologies, there is virtually no information in the published literature about the chemical speciation of inorganic compounds under actual processing conditions. This is primarily due to the lack of techniques that are capable of making in situ measurements of aqueous systems above 300°C. The ongoing x-ray-based studies are identifying the chemical species, oxidation states and ion pairing of inorganic compounds under extreme solvent conditions. It is imperative to make in situ measurements since we have shown that the chemical speciation is strongly dependent on temperature. Several complimentary techniques are being used in this study including x-ray absorption fine structure (XAFS), diffuse anomalous x-ray scattering (DAS) and vibrational (IR & Raman) spectroscopy. Thus, the results of this work are providing information critical to the calcining and vitrification of tank wastes. The results will also have a direct bearing on specific issues such as volatility of Tc (or Re) compounds and the complex chemistry of chromium compounds.

Research Progress and Implications

The following brief paragraphs summarize the most significant results after 2-1/4 years of the 3-year project. We have conducted measurements at 400°C of the oxidation of Cr (III) to Cr (VI) by NO_3^-/NO_2^-. These spectra are to the best of our knowledge *the first reported in situ spectroscopic observation of homogeneous aqueous redox chemistry at temperatures beyond the critical temperature of water (>374°C).* We also observed a time-dependence for the growth of the Cr(VI) XANES peak and have therefore obtained kinetic information for this redox system as well. We feel that these new techniques, if employed on actual waste components will elucidate the underlying chemistry.

In other studies we investigated the stability of aqueous ReO_4^- (surrogate for Tc compounds) to high temperatures (up to 400°C). The ReO_4^- was found to maintain the oxidation state VII regardless of a wide range of solution pH. ReO_4^- remained stable to 400°C even in the presence of the reducing agent NH_4^+.

We have also obtained information on the high-temperatures redox behavior of aqueous Cu^{2+}, another tank waste species that is prone to redox chemistry during high temperature processing. At high temperatures, Cu(II) has a strong tendency to be reduced to Cu(I) by reaction with other metal species. High temperature XAFS spectra of Cu(I) salts have shown the existence of an unusual ion-paired species that loses all waters-of-hydration .

Aqueous solutions of CrO_4^{2-} are known to undergo oligomerization reactions upon acidification. Isopolymetalates are also formed by the other row VI elements, Mo and W. These kind of polymerization processes are in general very common in aqueous solutions as they apply for the precipitation mechanism of hydroxides and oxides at basic pH conditions. As the first benchmark experiments we investigated the isopolytungstate system to high temperatures. The EXAFS spectra

are very rich in information and show large changes with both temperature and (starting) pH with a dramatic reduction in complexity between 200°C and 300°C. In order to better understand and quantify the observed spectral changes in the EXAFS we have turned to complimentary IR spectroscopic investigations. These IR measurements require a very short optical path length thus a new IR cell was specifically designed and built for this purpose. The combined results strongly indicate that besides the tungstate monomer a second, yet unidentified, species of simple geometry must be present at 300°C and starting pH value < 8. In contrast, recently acquired XAFS spectra of aqueous chromate solutions to low pH values and high temperatures show little change, indicating that the chromate remains tetrahedrally coordinated with little or no changes in the Cr-O bond distances throughout all investigated experimental conditions. We have also acquired IR spectra for the chromate system to high temperatures enabling us to compare the high temperature aqueous oligomerization chemistry between the row VI transition elements. These results are of high relevance to tank waste chemistry and have immediate applicability to resolving long-standing chemistry issues.

The project has supported the complete construction (finished Nov. 1999) of a device for DAS measurements of high temperature solutions at the APS. Measurements of radial distribution functions for high-temperature salt solutions (SrBr2 and NiBr2) are in progress. These types of studies complement the XAFS results by illuminating the full structure of contact ion pairing that has an effect on the kinetics and pathways of the inorganic chemistry that might be missed by XAFS. This device will also have importance in defining more completely the micro-structure in radionuclides in waste glasses to help access their long-term stability.

Planned Activities

A comprehensive study of chromate speciation from XAFS and FT-IR studies at temperatures to 425°C and pH from 1 to 13, will be completed in about 2 months. Anomalous scattering measurement of radial distribution function for the Sr2+ and Ni2+ systems will be completed by the end of this fiscal year. XAFS studies of vapor-phase Sr2+ species will also be completed by the end of the year.

List of Publications

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3. "Short-pathlength, High-pressure Flow Cell for Static and Time-Resolved Infrared Spectroscopy Suitable for Supercritical Fluid Solutions including Hydrothermal Systems", Hoffmann, M. M.; Addleman, R. S., Fulton, J. L., Rev. Sci. Instruments, 71, (2000), In press.
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5. "A Transition from a Six- to a Four-Coordinate Ni2+ Complex in High-Temperature Aqueous Solutions from X-ray Absorption Spectroscopy", Fulton, J. L.; Darab, J. G.; Hoffmann, M. M., Proceedings of the 13th International Conference on the Properties of Water and Steam, Tremaine, P. R., Hill, P. G. Irish, D. E., Balakrishman, P. V., Eds., NRC Press, Ottawa, 2000, In press.
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Dynamic Effects of Tank Waste Aging on Radionuclide-Complexant Interactions

Project ID: 59993

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Research Objective

The overall objective of this project is to provide a scientific basis for safely processing complexant-containing high-level tank wastes for disposal. Our key goals are to identify methods for preparing realistic complexant-containing tank waste simulants, and to use those simulants to determine the relative importance of organic complexants and their breakdown products on the partitioning of important radionuclides. Complexant-containing waste simulants are aged by various chemical processes and compared to samples of actual Hanford tank waste. This work will help to identify important aging processes in the tanks and provide the basis for developing successful treatment strategies.

Research Progress and Implications

This report summarizes work completed after 2.5 years of a 3-year project. Earlier in the project, we prepared, artificially aged, and analyzed simulants of tank AN-107 and SY-101 supernates, based on analytical data and historical records. During this phase of the project, it became clear that published analytical sample preparation methods were causing transformation of the organic compounds. Also, significant and unresolvable ambiguities in defining the source-term organic content of the wastes became apparent. The combination of these two problems led us to refocus our study of tank waste aging on the $^{99}TcO_4^-$ (pertechnetate) reduction that occurs in complexant-containing supernates. The reduced complexes of technetium that form as these wastes age are resistant to both conventional partitioning methods and to oxidative treatments. The mechanism(s) for pertechnetate reduction are unknown but could be radiolytic or thermal in origin.

Catalytic Reduction of Pertechnetate

The fission product metals ruthenium, rhodium, and palladium are well-known as potent catalysts, but their impact on nuclear waste aging has been overlooked. We prepared simplified simulants containing pertechnetate ion (0.1 mM), typical waste relevant organic complexants (50 mM each of EDTA, NTA, HEDTA, citrate, glycolate, and oxalate) and catalytic metals (1.0 mM each of Ru, Rh, Pd) in 2.5 M NaOH. Thermolysis of this simulant for 24 h at 65°C converted 99% of the ^{99}Tc activity to an insoluble black precipitate identified as hydrous TcO_2. In control experiments omitting catalytic metals or organic complexants, no reduction was observed. Probing the role of individual noble metals revealed that only ruthenium was an effective catalyst alone, but any combination of two catalytic metals produced extensive reduction of $TcO_4^{ñ}$ in 4 days. When the organics were probed individually under these conditions, glycolate, HEDTA and EDTA yielded >98% TcO_2. The addition of $Fe(NO_3)_3$ caused a substantial inhibition of the technetium reduction in the HEDTA and EDTA experiments, seemingly due to catalyst inhibition by Fe(III).

Hydrogen is a likely source of reducing equivalents and is known to be generated in complexant-containing tank wastes via thermal and radiolytic degradation of organic waste constituents. Complexant-free simulants were heated for 18 hours under flowing hydrogen gas, yielding >85% reduction of the pertechnetate using any of the three metal catalysts. Simulants containing gluconate,

a byproduct of sugar-based denitration processes at Hanford, trapped the reduced technetium as a soluble complex before TcO_2 precipitation could occur. The complex identical to the widely-used technetium radiopharmaceutical precursor $[TcO(gluconate)_2]^{n\tilde{n}}$ by UV-Vis.

In summary, we have shown that the chemical environment of complexant-rich tank wastes is sufficient to cause catalytic reduction of $TcO_4^{\tilde{n}}$, even in the absence of radiolysis. The transformation appears to involve a two-step process of complexant degradation to generate H_2, followed by catalytic reduction of pertechnetate to hydrous TcO_2 or soluble complexes. Given the evidence that fission product catalysis can dramatically impact the safe treatment and disposal of nuclear wastes, we concluded that further study of their abundance, distribution and reactivity in the waste is needed.

Catalytic Transformations of Organic Complexants

The Tc results led us to focus on the mechanism of chelator degradation, and how degradation products might effectively reduce other chemical species. In order to determine if hydrogen transfer was occurring under our reaction conditions, we prepared a typical basic simulant containing the three metal catalysts, one complexant, and cinnamic acid as a hydrogen acceptor. Proton NMR was used to analyze for hydrogenated cinnamic acid after thermolysis. The following relative scale of cinnamic acid reduction was observed: formate > gluconate > HEDTA > glycolate >>> EDTA, IDA, and glycine.

We next aimed to identify metal-mediated processes for EDTA degradation. Labeling the C-1 or C-2 position of the acetate groups with ^{13}C provided a direct NMR probe of intermediates and final products. In a standard 2.5 M NaOH simulant, no degradation of C-2 labeled ^{13}C-EDTA was observed in 5 days of thermolysis. However, partial degradation was noted when 1.0 mM $NaNO_3$ was added. At high nitrate concentrations (100 mM), significant ^{13}C-formate was observed, along with ^{13}C-carbonate. This indicates inhibition of transfer hydrogenation at high nitrate concentrations.

Simulants prepared at 5.0 M NaOH did not show any degradation of ^{13}C-EDTA, even in the presence of nitrate. At a lower concentration of 0.5 M NaOH, ^{13}C-formate is the major product, along with a small amount of carbonate, ethylenediaminetriacetic acid (^{13}C-EDA_3), and N,N'-ethylenediaminediacetic acid (^{13}C-EDA_2). The latter two likely degrade at a faster rate than the starting EDTA, and are presumably transiently formed in 2.5 M NaOH. The observation of formate is consistent with the slower rate of conversion of formate to carbonate at the lower pH. The reaction of C-1 labeled ^{13}C-EDTA was also investigated at 2.5 M NaOH in the presence of nitrate. Only a decrease in the carboxylate signal over time was observed, consistent with a decarboxylation process, releasing ^{13}C-CO_2. This confirmed that the aa-carbon of the acetic acid group serves as the exclusive source of carbonate.

Collectively, these observations support a process for EDTA degradation under alkaline conditions where three "hydride equivalents" are produced for each N-substituted acetic acid group that undergoes conversion to carbonate and carbon dioxide. Because only the initial EDTA breakdown step is slow, once the process is initiated it is possible to rapidly form 12 hydride equivalents, presumably leading to H_2 gas release or metal reduction. We are also examining an N-methylation reaction of amines in the presence of formate and formaldehyde, which may have broad relevance for the chemistry of organic amines in the waste.

Planned Activities

Year 3: Studies of the catalytic reactions will be closed out, with an emphasis on clearly establishing the relevance of the reactions to actual Hanford tank wastes.

Information Access

Six manuscripts are either submitted or in preparation. Preprints may be obtained by contacting the Principal Investigator.

Solvation Effects on Cesium Complexation with Calixarene-Crown Ethers from Liquid to Supercritical Fluids

Project ID: 65351

Chien M. Wai, University of Idaho

Research Objective

Supercritical fluid CO_2 is an alternative solvent for extraction of metals.[1] The solubility parameter of supercritical CO_2 varies with density resembling that of liquid hexane at moderate pressures in the supercritical region to those of chlorinated solvents at very high pressures.[2] By changing density of supercritical CO_2, the solvation environment of a metal chelate system can vary continuously and resembles over a wide range of solvents. Thus, supercritical CO_2 provides a unique system for studying solvation effects on metal chelation.

This project is designed to investigate the solvation effects on cesium complexation with macrocyclic compounds including crown ethers and calixarene-crown ethers in CO_2 from liquid to supercritical region at high pressures. A powerful spectroscopic technique for studying cesium chelation is nuclear magnetic resonance (NMR). Cesium has only one isotope, ^{133}Cs, with a nuclear spin I = 7/2. Popov et al. used NMR to study cesium complexation with crown ethers and cryptand.[3,4] Variation of the ^{133}Cs chemical shift as a function of the 18-crown-6/Cs^+ mole ratio in different solvents indicates that the solvent plays an extremely important role in the complexation process. The magnitude of the chemical shift upon cesium complexation with cryptand 222 (which has a tridimensional cavity) is much larger than with the flexible 18-crown-6. The NMR chemical shift for Cs^+ inside a cavity may be correlated to the configuration of the complex and the tightness of the fit.

Our collaborator, Clem Yonker at Pacific Northwest National Lab (PNNL), recently developed simple techniques for NMR studies in supercritical fluids.[5,6] In Yonker's method, a hand pump is used to deliver the desired high pressure and to transport the dissolved solute in a fused-silica tubing placed in the NMR probe. Because capillary tubing can stand very high pressures, this technique is safe and capable of performing NMR experiments up to several kilo-bars. Yonker's technique will be used to start our NMR experiments (proton, ^{19}F and ^{133}Cs) for studying cesium-crown ether complexation in supercritical fluids.

The solubility of crown ethers such as dicyclohexano-18-crown-6 is reasonably high in supercritical CO_2, $>1\times10^{-2}$ mol/L according to our preliminary data. The solubility of calixarene-crowns in supercritical CO_2 is much smaller, $<1\times10^{-3}$ mol/L. It is known that fluorination of ligand can significantly increase the solubility of metal chelates in supercritical CO_2.[7,8] To enhance the solubility of calixarene-crowns in supercritical CO_2, synthesis of fluorinated calixarene-crowns are currently underway in our laboratory. For simplicity, in the beginning of this project we chose to compare the complexation of cesium with crown ethers in conventional solvent systems and in supercritical CO_2 systems.

Research Progress and Implications

1. First extraction experiments

As a preliminary step, we began to investigate extraction of Cs^+ from an aqueous solution into chloroform using crown ethers as the extracting agent. The choice of chloroform lays in its low dielectric constant (4.8 at 20°C), similar to that of supercritical CO_2. Publications dealing with extraction of alkali metals (including cesium) into organic solvents of higher dielectric constant,

generally >10, have appeared.[9] However, there is no such study involving an organic phase of low dielectric constant.

In chloroform the solubility of Cs salts is very slight. This is in contrast to studies involving more polar solvents for which easily measurable concentrations of Cs salt in the organic phase could be obtained. Our studies so far have employed Cs picrate, which will subsequently be called CsX.

When an aqueous solution of CsX is equilibrated with chloroform containing an extracting ligand L, a series of equilibria will occur. First, the salt will be distributed between the two phases:

$$Cs^+_{(aq)} + X^-_{(aq)} \quad = \quad CsX_{(org)}$$

Because of the low dielectric constant of chloroform, ionization of CsX in the organic phase is negligible; the species should be considered to be an ion pair. This equilibrium will of course lie heavily on the aqueous side.

Next, interaction of CsX with the ligand L leads to a complex:

$$CsX_{(org)} + L_{(org)} \quad = \quad CsLX_{(org)}$$

Most of our work so far has employed the crown ether dicyclohexano-18-crown-6. With this ligand an additional equilibrium occurs:

$$CsLX_{(org)} + L_{(org)} \quad = \quad CsL_2X_{(org)}$$

These equilibria have been studied separately.

2. NMR measurements

Measurement of solution concentrations has been carried out by nuclear magnet resonance (NMR) using a Bruker DRX500 spectrometer available in the chemistry department, University of Idaho. Proton measurements were conducted at 500.13 MHz, and ^{133}Cs measurements were taken at 65.60 MHz. A high pressure system utilizing a hand pump and capillary tubing for NMR measurements in supercritical CO_2 is currently in construction.

3. The equilibrium $Cs^+_{(aq)} + X^-_{(aq)} \quad = \quad CsX_{(org)}$

Distribution experiments have been carried out using pure deuterated chloroform and aqueous CsX solutions with concentrations 0.01 M and lower. The two-phase system is agitated for 4 hours. Then the phases are separated by centrifugation for 2 hours. The proton NMR spectrum of the resulting organic phase is shown in Fig. 1. The features shown are a very small peak at 9.19 ppm representing the picrate ion and the residual $CHCl_3$ peak at 7.26 ppm. It turns out that the concentration of the picrate is most conveniently measured by comparison with the $CHCl_3$ peak. The latter is measured separately by adding a known amount of cyclohexane to the deuterated chloroform. $[CHCl_3]$ must be measured separately for each bottle of deuterated chloroform; it generally falls in the range 0.02-0.04 M. The areas of the picrate and $CHCl_3$ peaks are determined by Lorentzian deconvolution.

Results obtained so far indicate a linear relation between $[CsX_{(org)}]$ and $[CsX_{(aq)}]$ for low $[CsX_{(aq)}]$ (Fig. 2). The apparent falloff of $[CsX_{(org)}]$ at higher $[CsX_{(aq)}]$ requires further confirmation.

4. The equilibrium $CsX_{(org)} + L_{(org)} \quad = \quad CsLX_{(org)}$

The distribution experiment now includes the ligand L = dicyclohexano-18-crown-6. The tendency for complexation of CsX with this ligand is so strong that small amounts of the ligand must be used to study this equilibrium. The experiments conducted so far have used $[CsX_{(aq)}] = 0.01M$ and [L] in the range 0.008-0.0025 M. A portion of the proton NMR spectrum of one of these experiments is shown in Fig. 3. It shows a peak at 9.19 ppm representing CsX and a peak at 8.97 ppm representing CsXL. (It is possible that these species are hydrated to some degree; this issue has not been resolved.) Also shown is the residual $CHCl_3$ peak of the solvent. Again the relative concentrations of the Cs species are determined by Lorentzian deconvolution. The ratio of these to [L] is discussed below.

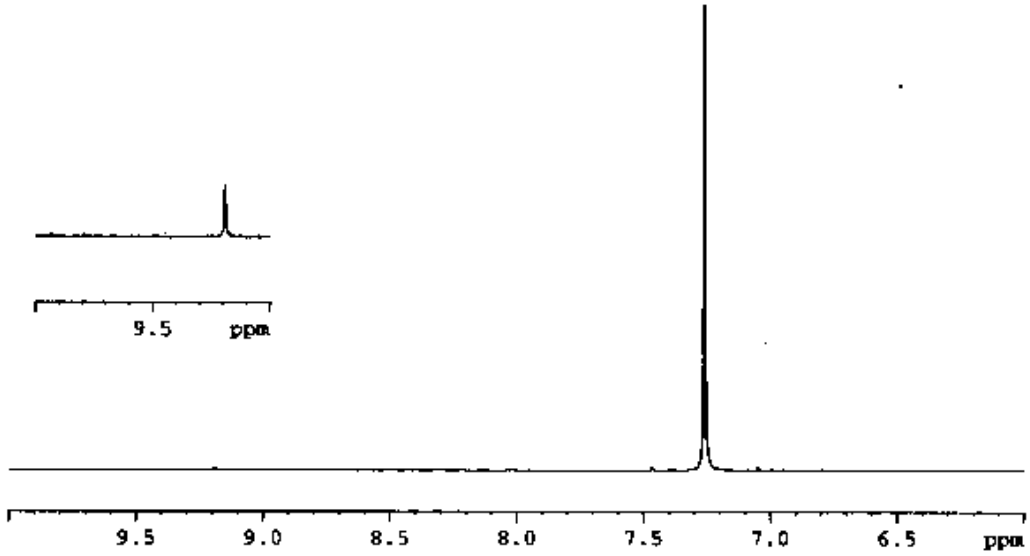
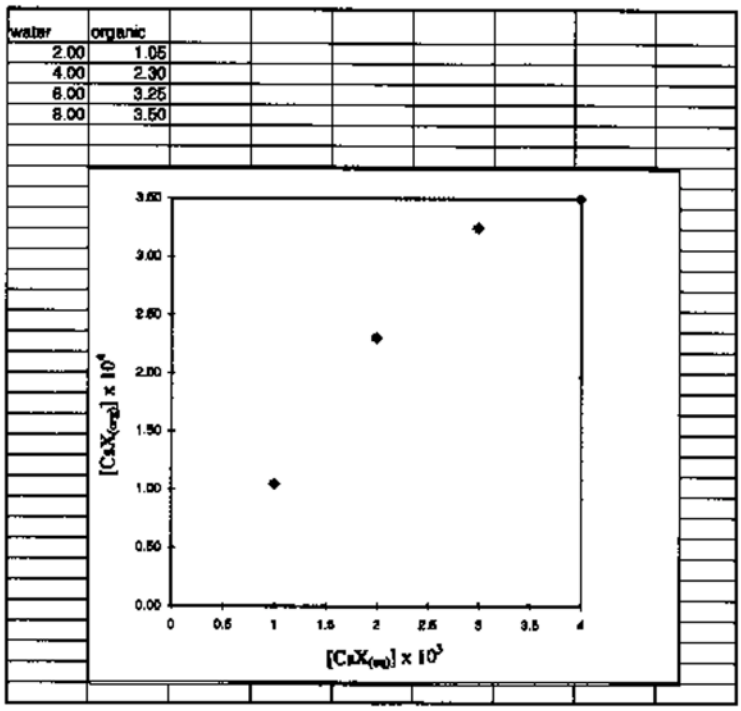


Figure 1. Proton NMR - extraction of 0.006 M Cs picrate into chloroform.



water	organic
2.00	1.05
4.00	2.30
6.00	3.25
8.00	3.50

Figure 2. Partition of Cs picrate between water and chloroform phases.

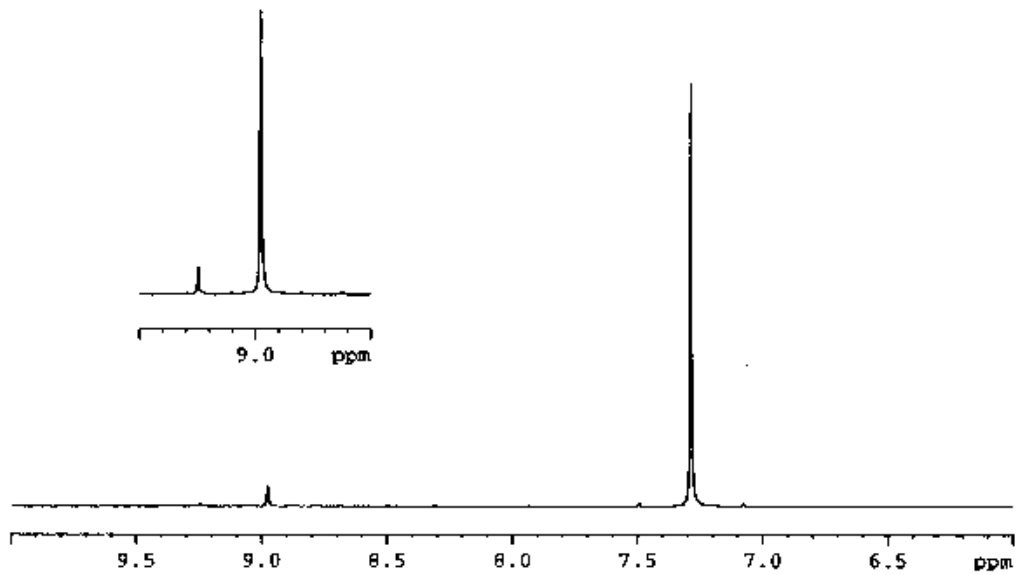


Figure 3. Proton NMR - extraction of 0.01 M Cs picrate into chloroform which is 0.001M in dicyclohexane-18-C-6.

From this spectrum the equilibrium constant K_1 = [CsLX]/{[CsX][L]} can be determined. Three measurements which we have made so far are in good agreement, giving $K_1 = 4.6 \times 10^5$. However, there is an inconsistency between these data and the results for the CsX partition experiments: namely, the concentrations [CsX] determined in the presence of the ligand should agree with those predicted from the partition experiments, but they do not. This difficulty remains to be resolved.

5. The equilibrium $CsLX_{(org)} + L_{(org)} = CsL_2X_{(org)}$

For higher concentrations of the ligand the quantity $[CsX_{(org)}]$ becomes negligible compared to the complexed forms. A typical proton NMR spectrum (with [L] = 0.2M) is shown in Fig. 4. The ligand resonances fall into two groups: a group of 20 protons centered at 3.7 ppm, and a group of 16 protons (present as 4 peaks of 4 protons each) centered at 1.5 ppm. The water peak, located at 2.83 ppm in this spectrum, shifts to higher field (lower ppm) at lower ligand concentrations. For the lowest concentrations, the water peak overlaps with the higher field resonances of the ligand. There is only one peak for the Cs species, indicating rapid exchange between CsLX and CsL_2X. Also shown on the figure are the areas of the spectral regions, determined by the normal area measurement routine in the NMR software. The ligand concentration is based on the low field ligand peaks, which are freer of interferences.

Because the Cs species are represented by only a single peak, the equilibrium constant K_2 = $[CsL_2X]/\{[CsLX][CsX]$ cannot be determined from the proton NMR spectrum. We have attempted to estimate K_2 by making use of the Cs spectrum. For [L] = 0.01 to 0.2 in the presence of $[CsX_{(aq)}]$ = 0.01M, the Cs spectrum consists of a single peak. The chemical shift of this peak, however, shifts with ligand concentration. This is shown in Fig. 5. For the range of chemical shifts shown, the relation is linear above [L]=0.01M.

There is an extensive literature on the variation of Cs chemical shifts with ligand concentration.[3,4] However, they generally involve organic solvents with high dielectric constants, for which relatively concentrated solutions can be prepared even in the absence of complexing ligands. In these circumstances it is possible to determine the Cs chemical shift for [L]=0. In the present situation, we would like to determine the chemical shifts for the pure species CsLX and CsL_2X. Then, the ratio of these species could be determined by interpolation. However, these chemical shifts are not directly available from Fig. 5. A fairly good estimate can be made for the shift of CsLX, but it is not at all

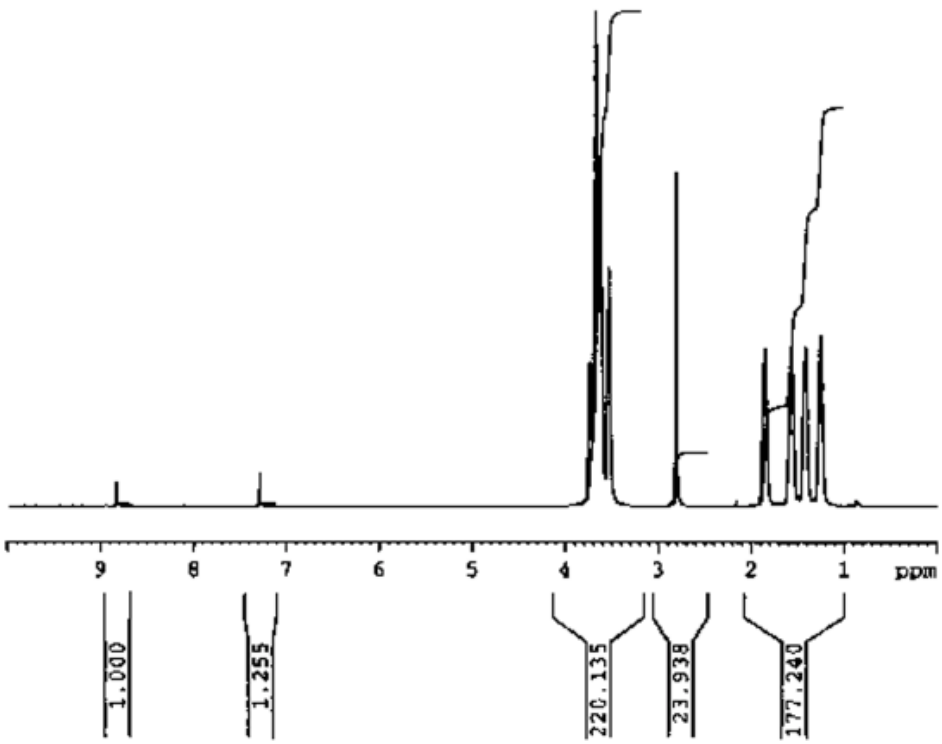


Figure 4. Proton NMR - extraction of 0.01 M Cs picrate into chloroform containing 0.2M dicyclohexano-18-crown-6.

clear when the trend of Fig. 5 will level off for high ligand concentrations so that the shift of CsL_2X can be determined. We are limited by the solubility of the dicyclohexano-18-crown-6 ligand.

Nonetheless, by making reasonable estimates we can guess at K_2. The values are relatively low, somewhere in the range 1-10. There is fairly good agreement between K_2 values obtained for different ligand concentrations for constant assumptions on the chemical shifts, indicating that this approach to measurement of K_2 is at least reasonable. At this point, however, the problem of measuring this constant is not resolved.

6. The role of water in the CsX-ligand equilibria

In an early set of experiments, we compared the introduction of CsX into a chloroform phase containing dicyclohexano-18-crown-6 by two methods: (1) equilibrating the chloroform phase with solid CsX, and (2) equilibrating the organic phase with an aqueous solution of CsX. We estimated the equilibrium constant K_2 from the proton and Cs NMR spectra, using consistent assumptions for the Cs chemical shifts of pure species. We found that K_2 differed by about an order of magnitude for the two circumstances. While differences are to be expected in general terms, we wanted to get a more detailed picture of the role of water in the equilibria.

To this end we are studying the equilibration of solutions of crown ethers in chloroform with a pure water phase, with no Cs salt present. Water has a slight but significant solubility in chloroform, about 0.05M. It turns out that the crown ether attracts water into the chloroform phase in proportion to the concentration of the crown ether, presumably by forming cryptands of the type H_2OL.

Fig. 6 shows the total water concentration $[H_2O]_{tot} = [H_2O]_{free} + [H_2OL]$ as a function of ligand concentration [L] of dicyclohexano-18-crown-6 in chloroform. The data can be fit to a straight line:

[L]	delta
0.2	-5.97
0.12	-3.26
0.1	-2.5
0.08	-1.8
0.06	-1.13
0.02	0.22
0.01	0.348

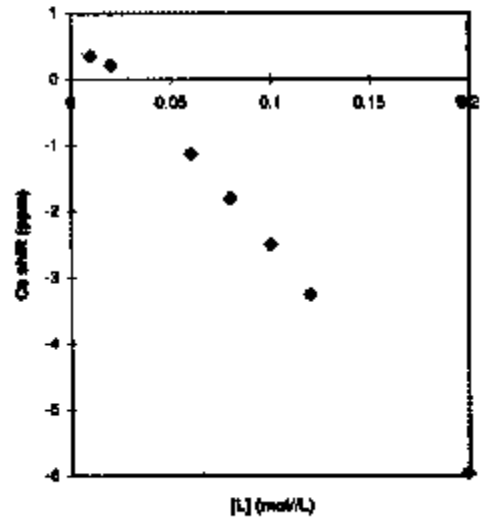


Figure 5. Relative Cs chemical shift vs. total ligand concentration for extraction of aqueous Cs picrate into chloroform containing dicyclohexano-18-crown-6.

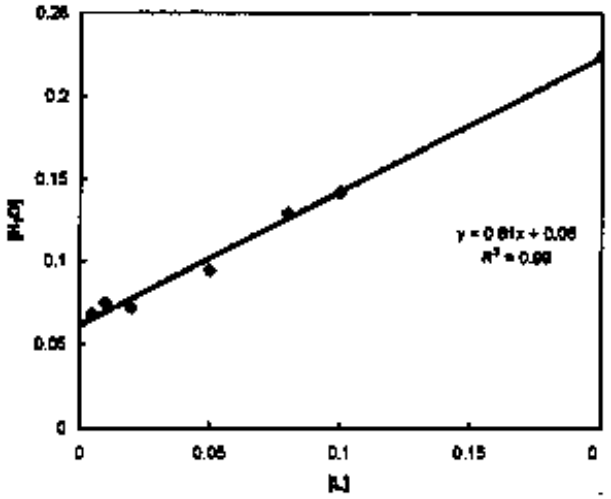


Figure 6. Total water concentration $[H_2O]_{tot}$ vs. ligand concentration [L] for extraction of pure water into a chloroform solution of dicyclohexano-18-crown-6.

$$[H_2O]_{tot} = 0.060 + 0.81[L]$$

In this equation, 0.060 represents the concentration of free water which will be constant because of the two-phase equilibrium with pure water. The figure 0.81 indicates that not all ligand molecules take up a water molecule: only 81% do.

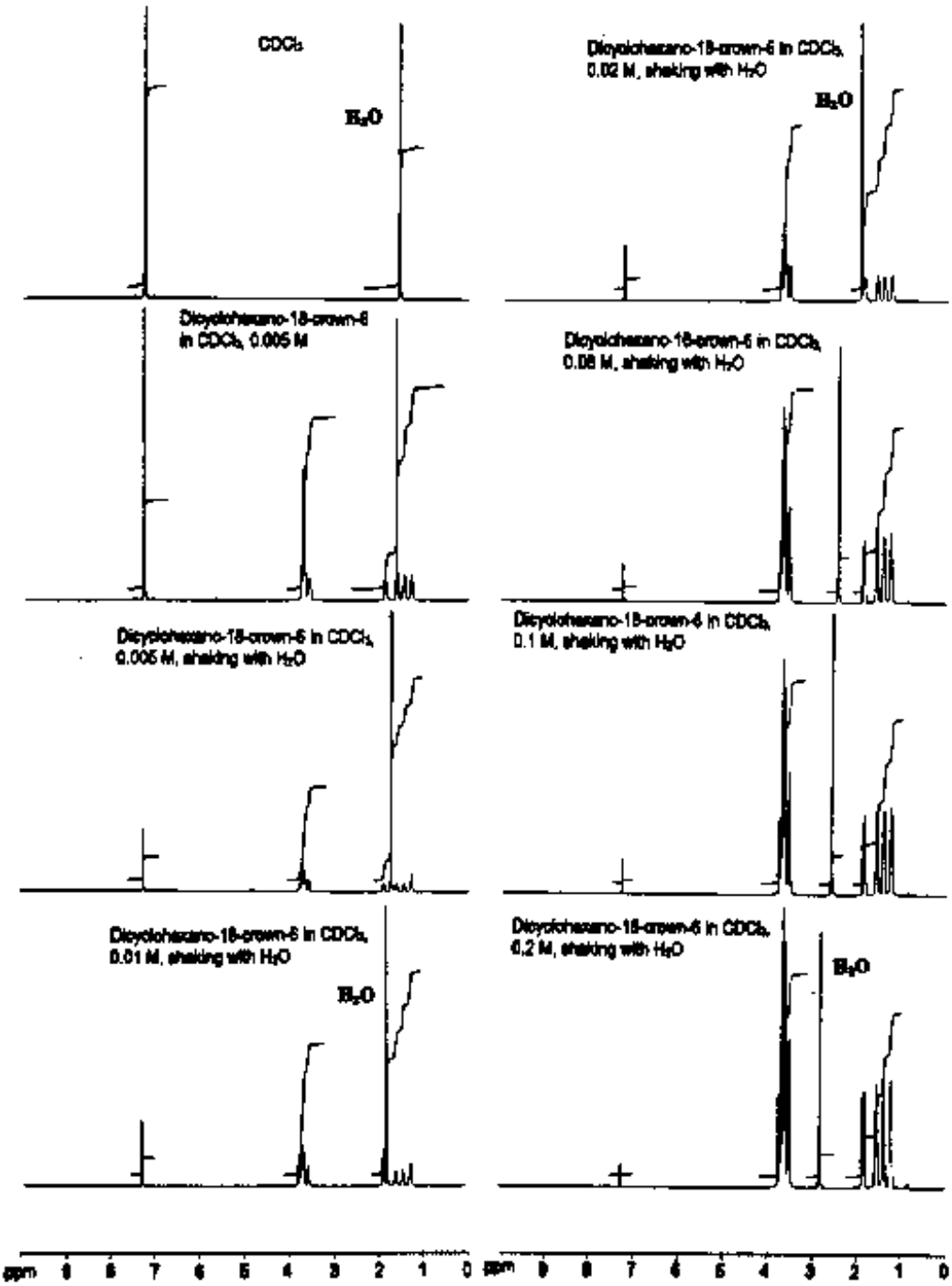


Figure 7. Proton NMR spectra of the chloroform phase after extraction of pure water into chloroform containing various concentrations of dicyclohexano-18-crown-6. The shift of water peak suggests a rapid exchange between free water and crown bound water.

This equilibrium is responsible for the variation of the water proton chemical shift with ligand concentration noted above. Figure 7 shows the water proton NMR chemical shift as a function of the crown concentration. The chemical shift suggests a rapid exchange between free H_2O and crown bound H_2O existing in the solvent. The result shows that evaluation of the equilibria involving Cs species in the extraction experiments must take account of the interaction of water with the extracting ligand. It is also possible that water interacts with the various Cs complexes, but that is yet to be determined.

As an offshoot of this project, we will study the extraction of water into pure organic phases (including eventually supercritical carbon dioxide) using various crown ethers.

7. Extraction of cesium with crown ethers in supercritical carbon dioxide

Some preliminary extraction experiments have been carried out to investigate the feasibility of extracting Cs^+ with supercritical CO_2 using crown ethers as extractants. The Cs^+-crown ether complexes are not soluble in supercritical CO_2. Our idea is to use a fluorinated counteranion to neutralize the charge of the complex and to transport the Cs^+-crown complex as an ion pair into supercritical CO_2. Because of the presence of fluorine atoms in the counteranion, the ion-pair may become soluble in supercritical CO_2. Preliminary results indicate that using pentadecafluoro-n-octanoic acid, $CF_3(CF_2)_6COOH$, or perfluoro-1-octanesulfonic acid tetraethylammonium salt, $CF_3(CF_2)_7SO_3[N(C_2H_5)_4]$ as a counteranion, Cs^+ in aqueous solutions can be extracted by supercritical CO_2 containing dicyclohexano-18-crown-6. The results will be presented at the forthcoming National ACS meeting to be held in New Orleans in August.

Planned Activities

We will start the supercritical fluid NMR studies this summer. The first system to be examined will be the crown ether/H_2O/CO_2 system to evaluate the differences between organic solvents and supercritical CO_2 for the $[H_2O]_{tot} = [H_2O]_{free} + [H_2OL]$ equilibrium. Crown ethers of different cavity sizes will be studied. It is known that crown ethers can carry water into the organic phase during liquid-liquid extraction, but the details of equilibration between free H_2O and crown ether bound H_2O in different solvents are not known. NMR provides an opportunity for us to look into this problem in detail. Supercritical fluid NMR study of this system as a function of fluid density will provide interesting information regarding the solvation effects on the H_2O-crown ether interaction.

The Cs picrate/crown ether/H_2O/CO_2 system will be examined next. We will continue our study of the Cs picrate/crown ether/ H_2O/$CDCl_3$ system to understand the equilibrium relations of the various Cs species involved. The effects of H_2O on Cs complexation with crown ether will be carefully examined in solvent and in supercritical CO_2 systems. Other counteranions including the perfluorinated carboxylic acid pentadecafluoro-n-octanoic acid will also be studied instead of picrate in the systems discussed above.

Proton NMR should be sensitive enough for the proposed NMR studies using the capillary tubing technique. ^{133}Cs NMR may not be sensitive enough for supercritical CO_2 studies because of the limited solubilities of regular Cs-crown ether complexes in the fluid phase. Some fluorinated calixarene-crown ethers should be ready for our tests this summer. It is hoped that the solubilities of the fluorinated calixarene-crowns will be sufficient for the proposed ^{133}Cs NMR studies.

We have also contacted Dr. J.W. Rathke of the Chemical Technology Division, Argonne National Lab, who is a well established scientist in high pressure NMR studies. The NMR probe used by Rathke's group at ANL is based on a toroid cavity resonator that provides signal-to-noise ratios which are superior to the solenoid and Helmholtz coils that are typically used in commercial NMR spectrometers. Dr. Rathke is interested in collaborating with us on the Cs complexation studies in supercritical fluids. In case we need a high sensitivity NMR probe for the proposed Cs study, we will work with Dr. Rathke at ANL for our NMR experiments.

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Potential Modulated Intercalation of Alkali Cations into Metal Hexacyanoferrate Coated Electrodes

Project ID: 60123

Dr. Daniel T. Schwartz, University of Washington

Research Objectives

Ions intercalate or deintercalate into metal hexacyanoferrate to maintain charge neutrality when iron centers in the matrix are reduced or oxidized, respectively. Nickel hexacyanoferrrate (NiHCF) is known to preferentially intercalate cesium over other alkali cations, thus providing a basis for separation. This program is studying potential-driven cation intercalation and deintercalation in metal hexacyanoferrate compounds, with the goal of (1) quantifying the ion exchange selectivity properties for cation mixtures, (2) enhancing ion exchange capacities, and (3) improving the material stability.

Research Progress and Implications

After approximately 2.5 years, progress has been made on each of the research objectives. A combined electrochemical and energy dispersive x-ray spectroscopy method has been developed for analyzing the quantity and type of ion loaded into NiHCF films. In the third journal article cited below, we describe the methodology and show the range over which this technique can be used to quantify separation factors in NiHCF coated electrodes. We find that the distribution coefficient for NiHCF coated electrodes can exceed $3x10^4$ ml/g in a solution of 10^{-6} M Cs^+ with excess sodium nitrate (1 M Na^+). This value for the distribution coefficient, which excludes the weight of the substrate, is comparable to values reported for bulk metal hexacyanoferrate compounds used in conventional ion exchange processes.

To increase the ion exchange capacity, we have taken three approaches, namely, cathodic deposition, spontaneous reduction, and sol-gel NiHCF/carbon/silica composite electrodes. In the first approach, NiHCF is deposited cathodically by cycling a platinum electrode between +850 and 0 mV vs. SCE at a scan rate of 25 mV/S in freshly prepared solution of 4 mM $NiSO_4$, 4 mM $K_4Fe(CN)_6$ and 500 mM Na_2SO_4. The resulting thin films can routinely be produced with ion intercalation capacities exceeding 8 mC/cm^2. Our normal anodic deposition scheme produces a typical capacity of 3 mC/cm^2, so cathodic deposition represents a roughly 3 fold improvement in capacity. In the same electrolyte, one can get films to form on a noble metal electrode by spontaneous reduction. If one places a noble metal in freshly prepared electrolyte overnight, the film that forms spontaneously normally has an ion exchange capacity in the range 5 to 20 mC/cm^2. A second layer will grow on the previous layer if fresh electrolyte is used. In this manner, through repeated spontaneous formation, we have made NiHCF films in excess of 33 mC/cm^2 of capacity (34.1 mC/cm^2 is our highest to date). This represents a ten-fold increase in capacity from the anodic films used at the beginning of this project. The third method, and the most immature, that has been developed to increase capacity is to make monolithic ceramic/carbon composite electrodes using sol-gel processing, followed by overnight soaking of the composite in a nickel sulfate/potassium ferrocyanide solution. This method, though not optimized at all, can also achieve greater than 20 mC/cm^2 of ion exchange capacity.

Finally, with regards to more stable materials, the sol-gel processed electrodes appear more stable in alkaline electrolytes than are normal NiHCF thin films made in any of the ways described above. Because the silica matrix of the sol-gel electrode is nano-porous and soluble in highly alkaline media, we find the electrode falls apart around pH 14, though some electrochemical activity was still displayed at that pH. Nonetheless, we are encouraged and believe this approach may work using other sol-gel ceramics that are less soluble at high pH.

Planned Activities

–Continue studies of selectivity, capacity, and the role of film processing.

–Assess cycle life characteristics of the various NiHCF electrode structures.

–Continue to characterize and optimize the material behavior and failure found in the sol-gel composite electrodes.

Information Access

(1) S.M. Haight, D.T. Schwartz, and M.A. Lilga, In-situ oxidation state profiling of nickel hexacyanoferrate derivatized electrodes using line-imaging Raman spectroscopy and multivariate calibration, *J. Electrochem. Soc.* **146**, 1866 (1999).

(2) D.T. Schwartz and S.M. Haight, Transport and chemistry at electroactive interfaces studied using line-imaging Raman spectroscopy, *Coll. Surf. A*, accepted.

(3) K.M. Jeerage and D.T. Schwartz, Characterization of cathodically deposited nickel hexacyanoferrate for electrochemically switched ion exchange, *Sep. Sci. Tech.*, submitted.

Complexants for Actinide Element Coordination and Immobilization

Project ID: 65378

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Research Objective

The goal of this project is to develop inorganic metal oxide clusters known as polyoxoanions (POAs) as complexants for the immobilization of actinide (*An*) ions from high-level waste (HLW). A diverse array of rugged isopolyoxoanions, $[M_xO_y]^{z-}$, and heteropolyoxoanions, $[X_aM_bO_c]^{d-}$, comprised of M = V, Mo, W and X = Si, P polyhedra will be investigated for their ability to incarcerate *An* ions. The research combines two objectives—*An*-POA coordination and *An*-POA containment. The first involves the synthesis, isolation, and characterization of POAs that can selectively bind *An* ions to form stable *An*-POA complexes in alkaline and acidic solutions. The second involves investigations of the thermochemistry of the *An*-POA complexes under vitrification conditions germane to the formation of proposed HLW forms, such as borosilicate glass. The approach is envisioned to provide two levels of *An* encapsulation for maximum stability and durability as well as the potential to incorporate higher levels of *An* ions (particularly Pu) in waste forms than now possible. Such versatility bodes well for the potential application of POAs as *An* complexants in technology of significance to the environmental management of HLW.

Research Progress and Implications

This report summarizes work performed since the commencement of the project on 1 October 1998. As an overview of the research progress to-date (15 June 1999), the strategic point is that selective binding of *An* ions by POAs depends upon the *An* valence. Actinide reduction-oxidation (redox) chemistry is a pivotal property in the proposed, rational use of POAs as coordinating ligands for *An* ions. Because POAs are oxidants and the transuranium elements are multivalent, the combined redox chemistry is rich and, oftentimes, confusing. The evidence of contrasting and conflicting valence behavior makes it difficult, if not impossible, to make broad generalizations about the collective properties of *An*-POA systems without appropriate experimentation. To illustrate this chemical diversity, we have prepared actinide complexes of two well-known series of heteropolyoxoanions—the Preyssler and Wells-Dawson anions. Research highlights follow below.

Preyssler anion, $[P_5W_{30}O_{110}]^{15-}$. Our previous work has shown that the Preyssler anion exhibits a preference for trivalent *An* and lanthanide (*Ln*) ions. Because we have yet to find a direct route for the preparation of $[An^{3+}P_5W_{30}O_{110}]^{12-}$, the incorporation of actinides into the Preyssler structure is done by exchange of Na^+ in $[NaP_5W_{30}O_{110}]^{14-}$. Based upon structural evidence for $[UP_5W_{30}O_{110}]^{11-}$,[Dickman et al., *J. Cluster Sci.* **1996** *7*, 567] the *An* ions are anchored to the internal surface of the tunnel by ten O atoms. Water molecules are also coordinated to *Ln*/*An* ions.[Soderholm et al., *J. Phys. Chem*. **1995** *99*, 9611]

Work Accomplished To-Date. We first examined the reactivity and behavior of Ce because of the stability of the Ce^{3+} and Ce^{4+} aquo ions as a prelude to experiments with U, Np, Am, and Cm. Even under conditions that are well-known to stabilize Ce^{4+}, the reaction of $H_4Ce(SO_4)_4$ with $[NaP_5W_{30}O_{110}]^{14-}$ results in the formation of the Ce^{3+}-exchanged Preyssler anion $[CeP_5W_{30}O_{110}]^{12-}$. Because both Ce^{4+}

and $[NaP_5W_{30}O_{110}]^{14-}$ are oxidants, the reduction of Ce^{4+} is remarkable. The reactivity of Ce stands in contrast to that of Np. Under identical conditions, the reaction of Np^{4+} with $[NaP_5W_{30}O_{110}]^{14-}$ does not lead to the encapsulation of either Np^{3+} or Np^{4+} within the molecular confines of $[P_5W_{30}O_{110}]^{15-}$. Instead, Np^{4+} is oxidized to $[NpO_2]^+$, which is not, in turn, encapsulated within the Preyssler tunnel structure. In the Np^{4+}-exchange reaction, the oxidation of Np may be catalyzed by $[NaP_5W_{30}O_{110}]^{14-}$, which is known to act as an oxidation catalyst. Under restricting conditions, the corresponding U^{4+}-exchange reaction with $[NaP_5W_{30}O_{110}]^{14-}$ is possible. Because the formal potentials indicate that Np^{4+} is more stable to oxidation than U^{4+}, we conclude that the Np^{4+}-exchange reaction should be possible. Consistent with this expectation is that, in addition to U^{4+}, Th^{4+} can be encapsulated.[Antonio et al., *J. Alloys Compd.* **1998** *271-273*, 846] From our initial experiments with hydrated actinide aquo ions, $An{\cdot}nH_2O$, we conclude that actinide redox chemistry, and not ionic size, is the pivotal issue with the use of the Preyssler anion for An^{3+} and An^{4+} complexation.

Wells-Dawson anion, $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$. A large collection of previous work has shown that this isomer readily accommodates both An^{3+} and An^{4+} ions in sandwich-like structures wherein one *An* is coordinated between two tetradentate $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ anions. Although no crystal structures of $[An(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{n-}$ (n=16 for An^{4+}, and n=17 for An^{3+}) anions are available, the *An* coordination is presumed to be 8-coordinate square antiprimatic. This geometry is exhibited in the crystal structures of the trivalent and tetravalent lanthanide species: $[Lu^{3+}(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ by Bartis [Ph.D. Dissertation, Hunter College of CUNY, 1997] and $[Ce^{4+}(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ by Molchanov et al.[*Sov. Phys. Crystallogr*. **1979** *24*, 96]

Work Accomplished To-Date. We examined the synthesis and properties of Ce complexes because of the stability of Ce^{3+} and Ce^{4+} ions in aqueous solutions before experimentation with U, Np, and Am. The burgundy-color Ce^{3+} complex $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ and the yellow Ce^{4+} complex $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ were prepared for cyclic voltammetry and bulk electrolysis measurements. Solutions of these anions are reversibly interconverted through a one-electron Ce^{3+}/Ce^{4+} redox process. Compared to the formal potential for the Ce^{4+}/Ce^{3+} couple in a noncomplexing electrolyte, the lower potential for the same couple in $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-/16-}$ indicates stabilization of Ce^{4+}. This stabilizing behavior was found to apply to Np^{4+}, which otherwise is rapidly oxidized by air to $[NpO_2]^+$ in water. Using the conditions employed for the Ce^{4+} studies, the reaction of Np^{4+} with two equivalents of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ produced a yellow solution and light-yellow microcrystalline solids. Optical spectroscopy results confirm the presence of Np^{4+}. Even after weeks of storage in air, oxidation of Np^{4+} was not evident. Cyclic voltammetry data revealed three redox waves. Two of these are consistent with the cyclic voltammetry of the uncomplexed $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ anion. We propose that the third wave is due to the one-electron reduction of Np^{4+} to Np^{3+}, similar to the one-electron reduction of Ce^{4+} to Ce^{3+} in $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-/17-}$. In order to probe the purported redox activity of Np^{4+}/Np^{3+} in $[Np(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-/17-}$, optical spectra were obtained (*ex situ*) for the yellow Np^{4+} solution complex and for the deep blue solution resulting from bulk electrolysis at reducing potentials. Although no evidence was found for Np^{3+} in this experiment, we plan to exploit the technique of *in situ* XAFS spectroelectrochemistry to elucidate the Np redox speciation.

Using the conditions established from the Ce^{4+} and Np^{4+} experiments, a violet solution and microcrystalline solids of $[U(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ were obtained from the reaction of U^{4+} with two equivalents of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$. Optical spectroscopy and XAFS results confirm the presence of U^{4+}. Even after months of storage in air, oxidation of U^{4+} was not evident. This indicates that U^{4+} is stabilized by coordination with the Wells-Dawson anion because, otherwise, in noncomplexing aqueous electrolytes U^{4+} is readily oxidized by air. XAFS data reveal that U^{4+} in $[U(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ has the same coordination environment in solid and solution. Cyclic voltammetry data obtained under reducing conditions show no evidence for a U^{4+}/U^{3+} redox couple. This is not entirely surprising in view of the very negative formal potential for the reduction of U^{4+}. Compared to Np^{4+}/Np^{3+} couple, U^{4+} is more difficult to reduce than Np^{4+}.

Planned Activities

We plan to follow up the leads mentioned in the research progress. In addition, we will commence the second objective of the program by testing the solubility of POAs in glasses. Our initial focus

will be on the immobilization of Preyssler and Wells-Dawson anion complexes. Phosphorus-31 NMR, luminescence spectroscopy, and XAFS will be employed to characterize the solid glass forms and solution precursor *An*-POA complexes.

Polyoxometalates for Radioactive Waste Treatment

Project ID: 54716

Dr. Michael T. Pope, Georgetown University

Research Objective

The research project has two major goals: (1) the selective sequestration of lanthanide (Ln) and actinide (An) cations, and technetium species, from tank waste solutions, using radiation-resistant and thermally-stable polyoxometalate anions as complexants, and (2) the conversion of complexed Ln/An/Tc to reduced oxide bronzes (e.g. M_xWO_3) under relatively mild conditions, and evaluation of the use of such bronzes as waste forms.

Research Progress and Implications

This report summarizes progress as of 31 January 2000, after 3.5 years of a 3-year project; i.e during a no-funds extension.

1. Selective sequestration of Ln^{3+}/An^{4+} by $[NaP_5W_{30}O_{110}]^{14-}$(**I**). The sodium cation that occupies the central cavity of this doughnut-shaped polyoxotungstate can be replaced only by cations of the same size, i.e. Ln^{3+}, An^{4+}(U →Cm), Ca^{2+}. *Other cations are excluded.* In aqueous solution (neutral or mildly acidic) at 160°, Nd^{3+} for example is incorporated in the presence of the major components of tank wastes, i.e. a 200-fold molar excess of Na^+, and in presence of Fe^{3+} and Al^{3+}. The encrypted metal cations are released by hydrothermal treatment under strongly acidic conditions. [Ref. 1, 3, 7]

"Preyssler" anion, M=Na

$[M^{n+}P_5W_{30}O_{110}]^{(15-n)-}$

2. New polytungstate complexes of Ln^{3+} and An^{4+}. The conditions of formation, structures, and stability of several new polytungstates as possible precursors to thermal conversion to tungsten bronzes (see below) have been determined. These include 1:1 and 1:2 complexes of the lacunary anion ligands $[P_2W_{17}O_{61}]^{10-}$ (**II**), and some very large assemblies incorporating multiple Ln cations. [Ref. 2, 5]

3. Polytungstate complexation of UO_2^{2+}. Uranyl (and other actinyl) cations are stable in aqueous solution under normal atmospheric conditions. The first examples of polytungstate complexes of UO_2^{2+} have been synthesized and structurally characterized. Examples include $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$ (**III**) and $[(UO_2)_3(H_2O)_6As_3W_{30}O_{105}]^{15-}$ (**IV**). Anion **III** is formed in solutions of high $[Na^+]$ and is extractable into organic solvents. [Ref. 6 and in preparation]

4. Conversion of tungstolanthanide and -actinide salts into tungsten bronzes. Under relatively mild conditions (N_2 or H_2 atmosphere, 500-700°C) ammonium salts of anions such as **IV** are cleanly converted into the cubic bronzes $(Ln/An)_xWO_3$. This method of synthesis represents a major improvement over conventional methods (ground mixtures of oxides and tungsten powder, ≥1000°C)

and is the subject of a patent application. The chemical stability of the bronzes as candidates for potential waste forms is currently under investigation. [Ref. 8]

5. Technetium recovery and storage. Initial investigations are being carried out with rhenium as a Tc-surrogate. Tungstorhenates incorporating Re(V) and Re(IV) have been characterized but polyniobates and niobotungstates offer the advantages of stability in alkaline solutions which constitute the majority of tank wastes. The first example of a nioborhenate(IV) complex, $[Re(Nb_6O_{19})_2]^{12-}$, has been isolated from alkaline solution but has proved difficult to crystallize for structural confirmation. Furthermore Re is slowly oxidized and released from this material. A much more promising strategy has recently been discovered. Alkaline (pH ~12) aqueous solutions of $Nb_6O_{19}^{8-}$ react with Re(I) carbonyl complexes under hydrothermal conditions to form $[Nb_6O_{19}Re(CO)_3]^{7-}$ (**V**) and $[Nb_6O_{19}\{Re(CO)_3\}_2]^{6-}$ (*syn* and *anti* isomers, **VI**). The new complexes have been characterized by ^{17}O NMR spectroscopy and single crystal X-ray structural analysis. The solid salts are thermally stable to 400°C (loss of CO, not Re) and are inert to oxidation. Known synthetic routes to M(I) precursor species such as $M(CO)_3^+$ from $Re(Tc)O_4^-$, and the variety of nucleophilic polyoxometalate anions available, suggest that complexes such as **V** and **VI** will prove to be excellent vehicles for separation and storage of Tc wastes.

Planned Activities

A renewal proposal describing the development of the recently-discovered Re/Tc polyoxoanion chemistry (see above) is to be submitted for a September 2000 start date.

Information Access

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2. "Self-Assembly of Supramolecular Polyoxometalates. The Compact, Water-Soluble Heteropolytungstate Anion $[As^{III}_{12}Ce^{III}_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$", Wassermann, K.; Dickman, M.H.; Pope, M.T., *Angew.Chem*., **1997**, *109*, 1513-1516; *Angew.Chem.Internat.Ed.Engl*., **1997**, *36*, 1445-1448
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5. "New Developments in the Chemistry of Heteropolytungstates of Rhodium and Cerium" Pope, M.T.; Wei, X..; Wassermann, K.; Dickman, M.H., *C.R.Acad.Sci*., **1998**, *1*, Ser.IIc, 297-304
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7. "Slow Proton Exchange in Aqueous Solution. Consequences of Protonation and Hydration within the Central Cavity of Preyssler Anion Derivatives, $[M(H_2O)\|\subset P_5W_{30}O_{110}]^{n-}$", Kim, K.-C.; Pope, M.T.; Gama, G.G.; Dickman, M.H. *J.Am.Chem.Soc.* **1999**,*121*, 11164 -11170
8. "Thermal degradation of Polyoxotungstates - An Effective Method for the Preparation of Tungsten Bronzes", Wassermann, K.; Pope, M.T.; Salmen, M.; Dann, J.N.; Lunk, H.-J., *J. Solid State Chem.* **2000**, *149*, 378-383

www.georgetown.edu/faculty/popem/poster.htm#poster

Removal of Technetium, Carbon Tetrachloride, and Metals from DOE Properties

Project ID: 60017

Dr. Thomas E. Mallouk, Penn State University

Sherman M. Ponder, Penn State University
John Darab, Pacific Northwest National Laboratory

Research Objective

The objective of this research is to prepare, characterize, and evaluate new materials and techniques for the removal of technetium (Tc) compounds, halogenated organics, cesium, and other troublesome metal ions from DOE waste streams and contaminated areas. One aspect of this work follows the discovery that nanoscale zero-valent iron and bimetallic iron-nickel particles, dispersed on high surface area supports, reduce metal ions (Cr, Hg, Pb, Cd and Re as a surrogate for Tc) and chlorinated organics to insoluble/innocuous forms much faster than does unsupported iron. A second aspect develops chemical separation techniques to improve on the tetraphenylborate (TPB) method for removal and disposal of cesium-containing wastes.

The scientific goals of the project are to better understand the surface chemistry and electrochemistry of the nanoiron reduction process, to develop supports that are compatible with a variety of mixed waste compositions, and to develop surface modifiers for supported iron that will optimize selectivity for the contaminants of interest. The support composition is of particular interest in the case of Tc separation and stabilization in the Hanford tank wastes, and in Tc removal from ion-exchange column effluents. In both cases the support material must be compatible with the vitrification process used in the final waste disposition. In the case of cesium removal, the research focus is to develop an understanding of the relevant liquid-liquid extraction processes and to develop continuous flow separation methods that minimize the formation of volatile and toxic byproducts from the TPB process.

Research Progress and Implications

This report summarizes progress in the third year of a 3-year collaborative project involving Penn State and Pacific Northwest National Laboratory (PNNL). Since the last report, we have studied detailed kinetics of the removal of Cr(VI), Pb(II), and tetrachloroethylene from aqueous solutions by various forms zero valent iron, and have obtained some kinetic data for removal of Tc(VII). We have coupled this with materials characterization and corrosion studies that show which forms are best for particular short- and long-term applications. An example of a short-term application is removal of Tc(VII) from tank waste or a column effluent; in this case high surface area, active materials are preferred. A long term application is removal of metal ions or chlorinated organics from groundwater; in this case, long-term corrosion resistance as well as moderately high activity are needed. We have also further developed methods for cesium disposal using TPB as a precipitating agent and liquid-liquid extraction to recover the cesium as an inorganic salt and reduce its contact time with TPB.

We previously demonstrated that nano-iron supported on zirconia removed significant quantities of TcO_4^- from simulated Hanford and commercial waste streams. More recent work has involved characterizing the Tc that has been sorbed onto this material using X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). In several tests, simplified waste and column effluent simulants containing TcO_4^- were contacted for approximately 24 hours, after which the separated materials were characterized. XANES results confirmed that the Tc sorbed onto

nano-iron/silica as well as the unsupported nanophase iron (in both simulants) was in a reduced form, most likely Tc(IV). EXAFS results on these same systems were similar, revealing that the Tc has 6 oxygen neighbors at 2.02 Å and approximately 3 Fe neighbors at 3.2 Å, i.e., that it exists in a mixed oxide phase. Another test that was performed contacted unsupported nanophase iron with a simulated waste containing NaOH, $NaNO_3$, and $NaNO_2$ at pH 13. Despite the presence of oxidizing nitrite ions, reduction/immobilization of the Tc still occurred. Control experiments using the silica support did not result in Tc removal. Corrosion studies comparing nanophase iron (supported and unsupported) and iron filings, which are much less active for metal and organic removal, show that the corrosion current density is lowest with unsupported nanoiron and is anodically controlled. The difference most likely derives from the formation of a thicker passive oxide film on the unsupported nano-iron than on the other forms. The details of this film formation are under investigation. Nanophase nickel-iron on carbon was found to be highly active for tetrachloroethylene (TCE) removal, and corrosion studies of this material are now in progress.

In light of recent events at the Savannah River Site, improved methods for separating cesium from TPB ions may have important implications for the process decisions currently being discussed. Benzene formation from the degradation of TPB exposed to radiation has currently halted the waste treatment process. Minimizing TPB exposure time should minimize benzene formation. Recently, we reported a batch extraction process that recovers cesium as CsCl and TPB as the sodium salt. While these were promising initial results, it was pointed out to us that chloride salts would present problems for vitrification/disposal of cesium, and that one of the solvents used in our process (acetone) could be problematic because of its volatility and flammability. Subsequently, we modified the process to use non-volatile, non-flammable solvents (dimethylsulfoxide or propylene carbonate). The new process involves an interesting three-phase (organic-aqueous-organic) liquid-liquid extraction and isolates cesium as the carbonate salt, free of TPB. TPB can be recovered from the denser organic phase, free of cesium. We are currently developing a continuous flow method in which two streams (TPB and dilute cesium waste simulant) converge at a plate-and-frame filter bed. This process minimizes the contact time of cesium and TPB, even for very large liquid volumes. The solids obtained in this process are then subjected to the liquid-liquid extraction procedure and the cesium is ultimately isolated as the carbonate salt.

Planned Activities

Work will continue on all aspects of the project described above. Initial results with Tc removal appear quite promising but must be followed up with more detailed experiments that elucidate the kinetics of the reaction, and the compatibility of the resulting solids with waste form processing. We intend to complete our materials and electrochemical characterization of various forms of supported and unsupported nano-iron, and also will complete our kinetic studies of metal ion and TCE remediation. Together these studies should provide a clearer prescription for matching a particular remediation material with a long- or short-term application. We will also continue work to understand the chemistry of the cesium recovery process, and to determine the projected utility of this process in DOE applications.

Information Access

Reprints/preprints of the following papers will be sent electronically upon request. Contact Tom Mallouk (tom@chem.psu.edu) or Melissa Pressler (scarlett@chem.psu.edu).

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Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste

Project ID: 59990

Dr. Norman C. Schroeder, Los Alamos National Laboratory

Professor Kenneth R. Ashley, Texas A&M University-Commerce
David L. Blanchard, Pacific Northwest National Laboratory

Research Objective

The ultimate goal of this project is to separate technetium from Hanford tank waste. Our prior work with Hanford Site tank waste indicates that the presence of complexants has produced unidentified, reduced technetium species not amenable to current separation technologies, or readily oxidized to pertechnetate. Consequently, we are synthesizing and characterizing some of the major classes of technetium complexes that may be formed under tank waste conditions. These complexes will be used as standards to characterize the non-pertechnetate species in actual wastes and to develop efficient oxidation or separation methods.

Research Progress and Implications

This report summarizes months 22-30 of a 37 month project. Initially, a series of known dimeric Tc(IV) complexes ($[(L)Tc(\mu\text{-}O)_2Tc(L)]^{n-}$) were prepared by the sulfite reduction of pertechnetate under mildly acidic conditions. Ligands examined included EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), DTPA (diethylenetriaminepentaacetic acid) and oxalate. None of these complexes exhibited significant stability under caustic conditions.

Using similar methodology, a second series of complexes were prepared under mildly caustic conditions using ligands such as IDA (iminodiacetic acid), EDDA (ethylenediamine-N,N′-diacetic acid), citrate, and glycolate. Although efforts to grow crystals suitable for x-ray crystallography have thus far been unsuccessful, the properties and structural details of these complexes has been at least partially elucidated using a variety of methods, including; UV-Vis, FT-IR, FT-Raman, NMR, x-ray absorption spectroscopy, and elemental analysis. These complexes typically decomposed within 24 hours in 2 M NaOH but the stability could be somewhat enhanced by mimicking the reducing environment in the tanks with the addition of excess reducing agent and free ligand.

Gluconate is a byproduct of sugar-based denitration processes at Hanford. Using sulfite or stannous chloride as a reductant, it readily forms a stable, reduced technetium complex at base concentrations of at least 2 M NaOH. This complex appears similar to the radiopharmaceutical precursor $[TcO(gluconate)_2]^{n-}$, that is often used as a transfer ligand complex when complexation of the ligand of interest is not competitive with TcO_2 formation and precipitation. Since TcO_2 formation is favored at high base concentrations for the other complexants studied, we have begun to study the ligand transfer reactions of Tc-gluconate with waste relevant complexants such as EDTA, NTA, EDDA, IDA. Any complexes formed will be examined for waste relevance.

It has previously been determined that at least some of the reduced Tc species in real waste are not retained by the Reillex HPQ resin, nor easily oxidized with peroxide. For this reason, a known quantity of the Tc-gluconate complex in 2.5 M NaOH was contacted with Reillex and the K_d determined. We found that although some of the complex adhered to the resin, a significant portion was not retained. When contacted with excess H_2O_2, the pink color faded to yellow. This stable yellow species is an unknown reduced Tc-complex that is not retained by Reillex.

In order to obtain greater insight into the nature of the non-pertechnetate complexes in actual waste we have tried to separate the species from an actual waste sample of AN–107 using Sephadex® G10 size exclusion gel. The total technetium analyses indicated that 60% of the technetium was coming through the column; a percentage consistent with the non-pertechnetate content of the AN-107 waste. The small pertechnetate anion adheres strongly to the top of the column.

Planned Activities

Future efforts are being directed towards further characterizing these complexes by UV-Vis, FT-IR, FT-Raman, and NMR. We are also preparing a shipment of samples for elemental analysis at Atlantic Microlabs in Georgia. In addition, ten samples were sent for XAS in Feb. and we are awaiting analysis of the data. These samples were of higher purity and concentration than our previous efforts. Preliminary capillary electrophoresis mass spectrometry (CE-MS) experiments with some rhenium and technetium complexes indicate this may be a powerful tool for the analysis of our complexes, as well as those found in real waste. Further experiments are planned.

Information Access

A poster presentation of this work will be made at the EMSP workshop in Atlanta in April and at the American Chemical Society meeting this March in San Francisco. Recent publications dealing with the technetium speciation and separation problems are listed below.

K. R. Ashley, G. D. Whitener, N. C. Schroeder, J. R. Ball, and S. D. Radzinski, in Progress in Metal Ion Separation and Preconcentration, ACS Symposium Series 716, A. H. Bond, M. L. Dietz, and R. D. Rogers, Eds., American Chemical Society, Washington, D C., 1999, p. 219.

K. R. Ashley, Jason R. Ball, Glenn. D. Whitener, Norman. C. Schroeder, and Susan. D. Radzinski, "Reillex™-HPQ Anion Exchange Column Chromatography: Removal of Pertechnetate Ion from DSSF-5 Simulant at Various Flow Rates", *SOLVENT EXTR. ION EXCH*., **17**, 1543 (1999).

K. R. Ashley, Glenn D. Whitener, Norman C. Schroeder, Jason R. Ball, and Susan D. Radzinski "Sorption Behavior of Pertechnetate Ion on Reillex™-HPQ Anion Exchange Resin from Hanford and Melton Valley Tank Waste Simulants and Sodium Hydroxide/Sodium Nitrate Solutions", *SOLVENT EXTR. ION EXCH*., **16**, 843 (1998).

Norman C. Schroeder, Susan D. Radzinski, Kenneth R. Ashley, Anh P. Truong, and Patrycja A. Szczepaniak, "Technetium Oxidation State Adjustment for Hanford Waste Processing," in *Science and Technology for Disposal of Radioactive Tank Waste*, N. J. Lombardo and W. W. Schulz, eds., Plenum Publishing Corporation, New York, NY, (1998).

Norman C. Schroeder, Susan D. Radzinski, Kenneth R. Ashley, Anh P. Truong, Glenn D. Whitener, "Feed Adjustment Chemistry for Hanford 101-SY and 103-SY Tank Waste: Attempts to Oxidize the Non-Pertechnetate Species," in preparation.

Radiation Effects on Transport and Bubble Formation in Silicate Glasses

Project ID: 60313

Dr. A. D. Trifunac, Argonne National Laboratory

I. A. Shkrob, Argonne National Laboratory
D. W. Werst, Argonne National Laboratory

Research Objectives

Vitreous borosilicate forms will be used for storage of HLW within the DOE complex. Our research aims to discover the chemistry induced by β and γ irradiation of mixed oxide glasses. The effects of radiation are studied from the standpoint of defect formation and transport properties. Special emphasis is made on aggregation of defects and formation of oxygen bubbles. The fundamental knowledge gained provides the needed scientific basis for extrapolating long-term behavior of stored radioactive waste glass forms.

The objectives are to understand the effect of ionizing radiation on point defect formation, to discover the mechanism for radiation-induced volatilization and devitrification, to determine the temperature, dose, and dose-rate effects, to assess the role of relaxation processes and diffusion.

Research Progress and Implications

This report summarizes work after two years of a three-year project. Over this time, we carried out a comprehensive EPR study of paramagnetic radiation-induced defects in borosilicate, silicate, and borate glasses. Several classes of such defects were examined and their structure and mechanisms for formation determined. Two papers were published in the Journal of Non-Crystalline Solids and one in the Journal of Chemical Physics.

Alkali borate glasses. Metastable electron and hole centers in boron trioxide and alkali borate glasses were studied using pulsed EPR and modeled with semi-empirical and ab initio methods. It was shown that electrons and holes in these glasses are trapped on valence alternation defects, undercoordinated oxygen (holes) and overcoordinated oxygen (electrons). This is the first experimental demonstration of such defects in oxide glasses. The local environment around these defects has major effect on spin parameters of the corresponding spin centers: All variants of oxygen hole centers are holes trapped on the nonbridging oxygen in a BO_3^- unit. Alkali cations and protons are excluded from this center; the hole is trapped on undercoordinated oxygen (the "O_1^-" defect). There is no clear distinction between different variants of the hole centers in alkali borate glasses. The observed difference in the spin parameters is due to variations of the immediate environment of the BO_3^- unit. The dangling bond center is an electron trapped on overcoordinated oxygen (the "O_3^+" defect). When the central oxygen is coordinated with borons, the neutral center is formed. If it is coordinated with an alkali cation or a compensated BO_3^- unit, a charged center is formed. The "O_3^+" defect is a deeper trap for electrons than an isolated network-bound alkali cation. Only clusters of alkali cations and network-bound protons can compete with this deep Coulombic trap.

Alkali silicate glasses. O- and Si-centered radicals in Li, Na, K and Cs silicate glasses were studied experimentally and theoretically. Irradiation of alkali silicate glasses results in the formation of oxygen hole centers (HC_1 and HC_2), silicon peroxy radicals, and a silicon dangling bonds. It was shown that in a subset of HC_1, the ≡SiO• radical is strongly coupled to a single alkali cation whose swinging motion causes asymmetric spin relaxation. It was shown that trapping of the hole by nonbridging oxygen atoms do not result in the release of the compensating alkali cation. The implication is that

irradiation of HLWF will not lead to mass migration of the modifier cations, as suggested by some researchers. In the oxygen hole center HC_2, there is rapid tunneling of the electron between two degenerate sites; this center is a hole trapped on a tetrahedral $=SiO_2^{2-}$ unit.

It is demonstrated that silicon peroxy radicals are formed by decay of self-trapped excitons; the same process yields Si dangling bonds. Our results identify this reaction as the main source of O_2 that eventually coalesces to form microscopic bubbles. The yield of oxygen is 10^2 to 10^4 times less than previously estimated. Radiation-induced volatilization of the glass appears to be much less a problem than was suggested in the past.

H atoms in oxide glasses. Radiolytic H atoms play important role in annealing the radiation damage. We were first to identify the formation mechanism for the H atoms at 300-500 K. The lifetimes of the H atoms were controlled by metastable spin centers. The H atoms migrated with diffusion constant of 1.5×10^7 cm^2/s (300 K) and activation energy of 0.13-0.16 eV. No kinetic isotope effect was found on the decay/diffusion of the H atoms, but there was a significant isotope effect on the H/D atom yield. This effect is comparable to the one observed in SiO_2:OH and aqueous acid glasses. This similarity indicates that in all of oxide glasses, mobile H atoms are generated via electron trapping at the proton(s) associated with three-fold coordinated oxygen. Semi-empirical simulations were used to estimate energetics of these electron-trapping reactions.

Planned Activities

Currently, we are focusing on two remaining problems: (I) the exact nature of spin centers in alkali borosilicate glasses and (II) the structure of hole centers in borate glasses with high modifier content (the latter is present as an inclusion phase in borosilicate forms). To address these problems, we will study ESEEM, ENDOR and high-frequency EPR of spin defects in several such glasses and reference crystals.

Information Access

1) I. A.Shkrob, B. M. Tadjikov, S. Chemerisov, and A. D. Trifunac, *Electron Trapping and Hydrogen Atoms in Oxide Glasses*, J. Chem. Phys. **111**, 5124-5140 (1999)
2) I. A. Shkrob, B. M. Tadjikov, and A. D. Trifunac *Magnetic Resonance Studies on Radiation-Induced Point Defects in Mixed Oxide Glasses. I. Spin Centers in B_2O_3 and Alkali Borate Glasses,* J. Non-Cryst. Solids **262**, 6-34 (2000)
3) I. A. Shkrob, B. M. Tadjikov, and A. D. Trifunac, *Magnetic Resonance Studies on Radiation-Induced Point Defects in Mixed Oxide Glasses. II. Spin Centers in Alkali Silicate Glasses,* J. Non-Cryst. Solids **262**, 35-65 (2000)

Development of Inorganic Ion Exchangers for Nuclear Waste Remediation

Project ID: 54735

Dr. Abraham Clearfield, Texas A&M University

Research Objectives

One of the most compelling environmental problems facing our nation is the remediation of enormous stocks of nuclear waste that exists throughout the land. The waste takes many forms, high level waste (HLW) stored in tanks, contaminated groundwater and soils and as solid sludge. We have attempted to address each of these problems.

Research Progress and Implications

One of the major techniques considered for remediation is the judicious use of ion exchange processes. We have concentrated on inorganic materials because they exhibit high selectivities for specific ions and because they are stable to the effects of radiation. In the past seven years we have received support from DOE initially through Battelle PNNL, then INEEL-Oak Ridge and through the EMSP. During that time we have synthesized about 50 ion exchange materials and characterized their ion exchange properties. In addition we have solved the crystal structures of the most crystalline exchangers and tracked the ion exchange processes by solving the structures of the partially and fully exchanged phases. This has led to a fundamental understanding of the exchange mechanisms from which we developed a theory that the selectivity for a particular ion is a function of ion size relative to the size of the tunnel or cavity present in the framework type exchangers. A prime example is that of sodium titanosilicate.

1. $Na_2Ti_2O_3SiO_4 \bullet 2H_2O$(CST). This compound is the most highly selective Cs^+ exchanger known and is also selective for Sr^{2+}. The structure of this compound was solved from powder data and found to have a framework structure enclosing unidimensional tunnels. For alkali metals the exchange sites were found to vary depending upon the size of the cation. Li^+ and Na^+ are small enough to fit into framework sites which accommodate half the required cations. The remainder lie within the tunnels. The larger Cs^+ cannot fit into the framework sites and can occupy only half the tunnel sites. Thus, only 25% of the total exchanger sites are available to Cs^+. However, the Cs^+ -O bonds that form are exactly equal to the sum of the radii for Cs^+ and O^{2-}. All other cations have a poorer fit and tend to be displaced by Cs^+. In the presence of Na^+ dual exchange occurs simultaneously as Na^+ fills the framework sites and a second site inside the tunnels. As the sodium ion concentration increases the uptake of Cs^+ site decreases to 0.05 - 0.1 meq/g in tank waste simulants.
2. Trisilicates: $M(I)_2M(IV)\ Si_3O_9 \bullet H_2O$, (M(I) = Na^+, K^+, M(IV) = Ti, Sn Zr, Ce). We have prepared a family of trisilicates and solved the crystal structures of three of them. These compounds have framework structures enclosing alternating large and small cavities. The cavity sizes vary with the size of the M(IV) cation. For example, the Ti phase does not take up Cs^+ but the Zr phase exhibits very high Kd values for Cs^+ (10^5 ml/g in groundwaters) and is even 1500 ml/g in 6M NaOH. The mixed phase $Na_2Zr_{0.75}Sn_{0.25}(Si_3O_9) \bullet H_2O$ shows even higher Kd values. The interchangeability of the M(IV) ion changes the size of the cavities and governs the selectivity. This is an excellent example of crystal engineering where substitutions within the framework change selectivities.

3. Pharmacosiderites: We have prepared a family of compounds based on the pharmacosiderite mineral structure, solved their structures and determined the ion siting.

The titanium silicate version, $K_3H(TiO)_4(SiO_4)_3 \bullet nH_2O$ has a structure that is similar to that of the CST compound. It exhibits a high affinity for both Cs^+ and Sr^{2+}.[7] The Kd values have been considerably improved by partial substitution of Ge for Ti, another example of controlling selectivity. The structure of the Sr^{2+} phase is under investigation.

Sodium Nonatitanate: This compound, of composition $Na_4Ti_9O_{20} \bullet nH_2O$ is layered and the interlayer spacing varies with the water content. It is selective for Sr^{2+} in highly alkaline systems and the strontium is easily eluted with mild acid solutions. It works well under column flow conditions and is stable to irradiation. The main interference is Ca^{2+}.

Summary of Additional Studies

4. We have developed a simple technique to remove Sr^{2+} from tank wastes that contain high levels of complexants. The scheme is to add a cation that is preferentially complexed and so releases the Sr^{2+} to the solution that is readily removed with our strontium selective sodium nonatitanate or CST. This really works!
5. We have prepared sodium micas and alumina and zirconia pillared clays that exhibit extremely high Kd values ($>10^5$) for Cs^+ in contaminated groundwater. They are superior to zeolites for Cs^+ removal and may be used as a barrier to Cs^+ movement in soils. The sodium mica traps the Cs^+ permanently.
6. We have prepared a sodium niobium silicate that appears to have a pyrochlore structure. It is highly selective for Sr^{2+} in the presence of Ca^{2+}, Mg^{2+} and Na^+.

Planned Activities

A major failing of the EMSP program is a lack of focus on actual remediation. We had almost no contact with people involved in the actual remediation. Although, we published more than thirty papers we received no inquiries or comments from any DOE personnel. Since we were not refunded, we cannot follow through on our theory of how to improve selectivity for targeted ions. Also, my team of post-docs and graduate students all left due to lack of funding.

In the interim we submitted a proposal on sludge treatment in collaboration with a team at CSIRO, Australia and phytoremediation with the Institute for Sorption and Problems of Endoecology (ISPE) in the Ukraine. Both were rejected. ISPE has demonstrated a 2-4 fold increase in radionuclides removal from contaminated soil at Chernobyl and CSIRO has shown that their process removes radioactive ions from heavy metal minerals. Unless some interest is shown in our work, I plan to move on to greener pastures such as nuclear medicine.

Ionizing Radiation Induced Catalysis on Metal Oxide Particles

Project ID: 54996

Dr. Michael A. Henderson, Pacific Northwest National Laboratory

Executive Summary

High-level radioactive waste storage tanks at DOE sites contain significant amounts of organic components (solid and liquid phases) in the form of solvents, extractants, complexing agents, process chemicals, cleaning agents, and a variety of miscellaneous compounds. These organics pose several safety and pretreatment concerns, particularly for the Hanford tank waste. Many currently proposed tank waste cleanup alternatives encounter potential safety and/or pretreatment problems associated with organics. Remediation technologies are needed that significantly reduce the amounts of problem organics without resulting in toxic or flammable gas emissions and without requiring thermal treatments. These restrictions pose serious technological barriers for current organic destruction methods, which use oxidation achieved by thermal or chemical activation.

This project focuses on a novel approach for destroying organics found in high-level mixed waste prevalent at DOE sites. In this project, we have studied the destruction of organics, such as those found in Hanford tank waste, using reduction/oxidation (redox) chemistry resulting from exposure of typical photocatalytic materials to ionizing radiation (e.g., gamma radiation). Conceptually, this process is an extension of photocatalytic processes known to occur with visible and ultraviolet (UV) light at the interfaces of metal oxide photocatalysts (such as titanium dioxide, TiO_2). In these processes, energy is absorbed by the photocatalyst from light resulting in electron being excited within the photocatalyst. The excited electrons become available for reaction with solution species such as water, while the 'holes' (electronic states in the photocatalyst previously occupied by the excited electron) then strip electrons from adsorbed organic species resulting in oxidative destruction of the organic. The energy separation between the hole and the excited electron reflects the redox capability of the excited electron/hole (e^-/h^+) pair, and is dictated by the energy of the incident light and the electronic properties of the photocatalyst. Unfortunately, application of visible or UV light to large scale photocatalytic processes is severely limited by their marginal transparency into most metal oxide catalysts. Additionally, the relatively weak photon energies of visible and UV light limit the types of metal oxide catalysts that can show results. The use of ionizing radiation overcomes optical transparency limitations associated with visible and UV light (e.g., gamma-rays penetrate much farther into materials than either visible or UV light) and permits the use of wider variety of metal oxide catalysts that opens the door to a potentially greater degree of redox capabilities than those photocatalysts that can only be used with visible or UV light. The use of ionizing radiation offers several attractions. For example, the process operates at ambient temperature and pressure eliminating many safety concerns associated with hydrothermal or calcination approaches. The metal oxide catalysts are robust and stable in both radiation chemically corrosive environments. Another advantage of this approach is that conceptually no additional safety concerns other than those required for handling mixed waste should be required, and existing radiation sources available at the Hanford Site, specifically, ^{137}Cs capsules, could be employed

In the three years of this program, we examined in detail the radiocatalytic destruction of EDTA, a typical chelating agent found in DOE tank waste, over various TiO_2 catalysts. Our results show that exposure of solutions containing EDTA and TiO_2 to gamma radiation resulted in significant catalytic destruction of EDTA over that observed in absence of TiO_2. This is as the case under conditions that might be encountered with tank waste (high pH, high electrolyte concentration and with the presence of chelating cations such as strontium). The mechanism for this destruction however

does not appear to be the same as that of UV-based photocatalysis. We have conducted similar studies on smaller probe organic molecules (such as ethanol, formic acid, and acetic acid). UV-based experiments do show significant destruction of these small organics, in agreement with the literature, whereas our results show that solution-phase radiolytic processes dominate those associated with the TiO_2 surface to the extent that any catalytic effects are not detected. Therefore, we conclude that organics can be destroyed over typical metal oxide photocatalysts using ionizing radiation as the light source. However, the mechanism and viability of this approach have not been determined.

On fundamental side, this project has significantly added to the fields understanding of how ionizing radiation interacts with metal oxides and initiates chemical processes at their interfaces. This project has been highly productive in term scientific output and collaborations. To date, this project has resulted in approximately 10 publications in peer reviewed journals, with at least 5 additional manuscripts under review or soon to be submitted. Results from these works have been presented at over 15 national and international scientific meetings and at invited talks at 5 academic institutions (Univ. of Washington, Univ. of Illinois, Univ. of Puerto Rico, Notre Dame Univ. and Texas A&M Univ.). As a result of this project, collaborative interactions have been developed between PNNL and the following institutions: Univ. of Puerto Rico, Univ. of New Mexico, Univ. of Zurich and New Mexico Tech.

Modeling of Spinel Settling in Waste Glass Melter

Project ID: 65422

Dr. Pavel Hrma, Pacific Northwest National Laboratory

Petr Schill, Glass Service, Ltd.
Lubomir Nemec, Institute of Inorganic Chemistry
Jaroslav Klouzek, Institute of Chemical Technology
Martin Mika, Institute of Chemical Technology

Research Objective

Determine the fraction of spinel in molten HLW glass that is compatible with low-risk melter operation. To this end, investigate spinel behavior in HLW glass and obtain data to be used in a mathematical model for spinel settling in a HLW glass melter. Modify the current glass-furnace model to incorporate spinel settling.

Research Progress and Implications

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 crystals 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
- 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 model.

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

Spinel crystals form during the initial melting stages, precipitating from the nitrate melt within the bed of reacting melter feed. Spinel formation starts at temperatures above 400ºC and peaks at 650ºC, the temperature at which the nitrate decomposition is nearly complete and the glass-forming melt is established. Though these crystals usually dissolve in the glass-forming melt during the final stages of conversion, spinel forms again 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 concentration of some minor waste components, such as RuO_2 and Ag_2O, and may vary from 1 to 10^4 crystals per mm^3. As a result, spinel crystal size varies from 1 to 100 µm.

Laboratory studies of spinel formation must consider that spinel crystallization is a strong function of the temperature history and that surface crystallization may affect crystallization kinetics in powdered glass.

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. The rate of spinel growth and dissolution has been measured under conditions similar to those in the melter. At low viscosity, when crystals move within the melt by buoyancy, the rate of dissolution of spinel is constant at constant temperature and exhibits a non-Arrhenius dependence on temperature. Measurements of crystal growth at low melt viscosity indicate that the growth rate does not drop to zero as temperature approaches liquidus. This is contrary to what has been reported in the literature. (See for example, H. Scholze, Glass, Springer, New York, 1991.) At higher viscosity, when waste glass is in the canister, the kinetics of spinel crystallization follows the Avrami equation with Avrami exponent 0.8. This is a low value, attributable to the impinging of concentration layers.

The concentration of spinel in the melt depends on melt temperature, composition, and redox. These functions were expressed in the form of constitutive equations to be used not only in melter models, but also in models for glass formulation, waste retrieval, blending, and pretreatment. These results have a potentially significant impact on Hanford HLW vitrification schedule and cost.

Planned Activities

- measure spinel response to a typical temperature history computed for a HLW glass melter
- study spinel settling under laboratory conditions as a function of temperature
- develop models for predicting the fraction of spinel that settles during HLW glass processing
- study the effect of spinel sludge aging on its rheological behavior

Information Access

The following papers have been published, are in print, or in final stages of preparation:

1. M. W. Stachnik, P. Hrma, and H. Li, "Effects of High-level Waste Glass Composition on Spinel Precipitation," *Ceram. Trans*. 107 (1999).
2. M. Mika, J. V. Crum, and P. Hrma, "Spinel Precipitation in High-Level Waste Glass," *Proceedings of the 5th ESG Conference,* Prague, Czech Republic 1999.
3. M. Mika, P. Hrma, and M. J. Schweiger, "Rheology of Spinel Sludge in Molten Glass," *Ceramics-Silikaty* (accepted).
4. P. Hrma :Modeling of Spinel Settling in Waste Glass Melter." *In Science to Support DOE Site Cleanup*, Pacific Northwest National Laboratory, PNNL-12208 UC-2000 (1999).
5. P. Izak, P. Hrma, M.J. Schweiger, "Nonisothermal crystallization of spinel from a high-level waste feed," submitted to ACS proceedings.
6. P. Schill and P. Vlcek, "Mathematical Model of Radioactive Waste Glass Melter, 5th International Seminar on Mathematical Simulation in Glass Melting," Horni Becva, Czech Republic, June 17-18,1999, Proceedings, p.112-118
7. P. Schill, A. Franek, M. Trochta, P. Viktorin, and P. Vlcek, "Integrated Glass Furnace Model, 5th International Seminar on Mathematical Simulation in Glass Melting," Horni Becva, Czech Republic, June 17-18,1999, Proceedings, p.125-137.
8. P. Hrma, J. D. Vienna, J. V. Crum, G. F. Piepel, and M. Mika, "Liquidus Temperature of High-Level Waste Borosilicate Glasses with Spinel Primary Phase," *Mat. Res. Soc. Proc.* (2000).
9. J. Alton, T. J. Plaisted, and P. Hrma, "Crucible Study of Spinel Settling in High-Level Waste Glass," Ceramic Transactions (to be submitted).
10. P. Izak, J. Klouzek, and P. Hrma, "Evolution of crystalline Phases during High-Level Waste Feed-to-Glass Conversion," Ceramic Transactions (to be submitted).
11. T. J. Plaisted, J. Alton, P. Hrma, and B. Wilson, "Spinel Nucleation and Growth in High-Level Waste Glass," Ceramic Transactions (to be submitted).
12. P. Izak, P. Hrma, J. D. Vienna, and B. Wilson, "Effect of Oxygen Partial Pressure on Liquidus Temperature with Spinel Primary Phase," Ceramic Transactions (to be submitted).
13. T.J. Plaisted, F. Mo, B. Wilson, and P. Hrma, Surface Crystallization of Spinel and Acmite in High-Level Waste Glass," Ceramic Transactions (to be submitted).

Radiation Effects in Nuclear Waste Materials

Project ID: 54672

Dr. William J. Weber, Pacific Northwest National Laboratory

Research Objectives

Radiation effects from the decay of radionuclides may impact the long-term performance and stability of nuclear waste forms and stabilized nuclear materials. Thus, the research performed under this project has significant implications for the High-Level Waste and Nuclear Materials focus areas within the current DOE/EM mission. In the High-Level Waste (HLW) focus area, the results of this research will lead to improvements in the understanding of radiation-induced degradation mechanisms and effects on dissolution kinetics, as well as predictable models for waste form performance. In the Nuclear Materials focus area, the results of this research will lead to improvements in the understanding of radiation effects on the chemical and structural properties of materials for the stabilization and long-term storage of plutonium, highly-enriched uranium, and other actinides. Consequently, this research will result in improved glass and ceramic waste forms for the immobilization of high-level tank waste, plutonium residues and scraps, surplus weapons plutonium, and other actinides.

This research project is investigating radiation effects in glasses and ceramics at the atomic, microscopic, and macroscopic levels. By using experimental and computer simulation approaches, this research endeavors to develop the underpinning science and models necessary to assess radiation effects on the performance of glasses and ceramics designed for the immobilization of high-level tank waste and nuclear materials. The ultimate objective of this project is to provide the scientific understanding and rationale for developing improved glass and ceramic waste forms and to develop scientifically based predictive models for the performance of nuclear waste forms and stabilized nuclear materials.

Research Progress and Implications

This report summarizes work after 3 years of a 3-year project. Work to date has resulted in 35 publications and papers in preparation. Highlights of the research are presented below.

Radiation effects in three compositionally identical Pu-doped (1 wt %) simulated waste glasses, with varying (239/238) isotopic ratios, have been studied. The radiation dose in these glasses is equivalent to 20, ten thousand, and one million years, respectively. Changes in density, stored energy, local structure, and valence states have been determined. The results indicate that the accumulation of defects giving rise to the stored energy precede the rearrangement of the glass network that manifests as volume changes. The stored energy could enhance dissolution kinetics. Electron spin resonance measurements indicate no evidence for radiolytic decomposition into oxidizers or reduced elements.

Detailed experimental and computer simulation studies of radiation effects and annealing in Pu-containing zircon (10 wt % Pu-238) have been performed. Alpha decay induces a crystalline to amorphous transformation, in which both long-range order and edge-sharing relationships between SiO_4 and ZrO_8 polyhedra are lost, leading to 18.4% swelling. Computer simulation of the amorphization process is in excellent agreement with experimental results. A tentative model of amorphization over geologic time periods has been developed. Annealing studies indicate that decomposition into constituent oxides should not occur under repository conditions.

There is a critical lack of understanding regarding ionization effects from beta decay on nuclear waste glasses. Borosilicate glasses are known to be sensitive to ionization damage above a threshold dose. To study ionization effects under more realistic conditions, seven different glasses have been irradiated at relevant temperatures (50, 100, 150, and 200°C) over 2.5 years with gamma radiation to doses of 25, 75, and 150 MGy. The highest dose is only equivalent to about 25 years of storage for

DOE HLW glasses, which indicates the difficulty in performing realistic testing. To date, changes in volume are negligible. Minor changes in the Raman, polarized-Raman, and FTIR spectra are observed. Significant changes, which are believed to be due to electronic defects, are observed in UV-Vis-NIR optical absorption spectra of the sodium-borosilicate glass compositions. Some changes in Fe oxidation states have been observed.

Single crystals of synthetic $ZrSiO_4$ and polycrystals of $A_2Ti_2O_7$ pyrochlores (A=Y, Sm, Gd, Lu) have been irradiated with different ions over a wide range of temperatures to develop kinetic models of radiation effects. The results of these studies show that amorphization in these materials is a complex process controlled by a variety of parameters that impact long-term performance models. For both systems, the data suggest that irradiation with light ions (helium through xenon) may not provide accurate simulation of the dose dependence of amorphization due to α-decay events. In the case of the pyrochlores, there is no significant effect of the A-site cation on the kinetics of amorphization, and there is excellent correlation with data from studies of actinide-doped pyrochlores. However, a significant effect of A-site cation on the dissolution kinetics of as-prepared samples was observed, and the results suggest incongruent leach of the Gd, Lu, and Y relative to Ti. Irradiation-induced amorphization increased the dissolution kinetics of $Gd_2Ti_2O_7$ and $Lu_2Ti_2O_7$ by at least an order of magnitude, which is consistent with the observed increase in Cm and Pu release kinetics in an actinide-doped pyrochlore.

Ionization from beta decay during interim and early storage (<500 years) can significantly impact the structure and properties of nuclear waste glasses. Much of this impact comes from the longer-lived electronic excitations, known as self-trapped excitons. The decay of self-trapped excitons can lead to permanent defects, and the presence of self-trapped excitons can lead to significant changes in the migration energetics for defects or the diffusion of incorporated radionuclides. A computational framework to study these processes did not exist prior to this project but has been developed using DFT, *ab initio*, and semi-empirical methods.

Molecular dynamics (MD) simulations have been used to determine threshold displacement energies in MgO (a test case) and $ZrSiO_4$. The MD simulations have revealed the dynamic nature of atomic displacement processes in these oxides. The migration energies for native vacancies in $ZrSiO_4$ have been determined by energy minimization methods. Results show that both zirconium and oxygen vacancies readily migrate, which may assist damage recovery processes. Energy minimization methods have also been used to determine the energetics of Pu^{3+} and Pu^{4+} incorporation in zircon to identify the most stable defect configuration for each oxidation state and to assist in the interpretation of XAS data. These computational capabilities are available to other EMSP, EM, and DOE projects to determine the energetics of radionuclide incorporation and self-diffusion in different nuclear waste forms and phases.

Planned Activities

The above research efforts have been phased out. The only ongoing activity is the preparation of publications related to work accomplished over the initial 3-year term of this project. A renewal proposal has been submitted to continue this effort, an important aspect of which is dissolution measurements of samples that have been characterized during the initial 3-year term.

Radiation Effects on Materials in the Near-Field of a Nuclear Waste Repository

Project ID: 54691

Dr. Lu-Min Wang, University of Michigan

Prof. Rodney C. Ewing, University of Michigan

Research Objective

Site restoration activities at US DOE facilities and the permanent disposal of nuclear waste generated at DOE facilities require working with and within various types and levels of radiation fields. Once the nuclear waste is incorporated into a final form, radioactive decay will decrease the radiation field over geologic time scales, but the alpha-decay dose for these solids will still reach values as high as 10^{18} alpha-decay events/gm in periods as short as 1,000 years. This dose is well within the range for which important chemical (e.g., increased leach rate) and physical (e.g., volume expansion) changes may occur in crystalline ceramics. Release and sorption of long-lived actinides can also provide a radiation exposure to backfill materials, and changes in important retardation properties (e.g., cation exchange capacity) may occur. The objective of this research program has been to evaluate the long-term radiation effects in materials used in processing high-level nuclear waste or materials in the near-field of a nuclear waste repository.

Research Progress and Implications

As of February, 2000, ninety percent of the originally proposed work has been completed. Since the project was delayed due to the move of both PI and co-PI from University of New Mexico to University of Michigan in 1997, a no-cost extension to 5/14/2000 has been requested by the PI and approved by DOE.

The long-term radiation effects in concerned materials have been evaluated with accelerated laboratory experiments utilizing energetic electrons and ions, which include *in situ* transmission electron microscopy (TEM) during irradiation using the HVEM/IVEM-Tandem National Facility at Argonne National Laboratory as well as ion exchange studies. The materials studied included: zeolites, layered silicates (smectite clays and mica), as well as crystalline silicotitanate (CST). CST is an important ion exchange material proposed for use in the chemical separation process of high-level liquid radioactive wastes (HLW).

In situ TEM has shown that all the studied materials (i.e., zeolites, mica, smectite clays and CST) are susceptible to irradiation-induced solid-state amorphization (i.e., the materials' unique sheet or porous crystalline structure is completely destroyed by irradiation). Amorphization can either be induced by ionization processes (as occurs with β- or γ- irradiation) or by direct displacement damage processes (as by α-recoils). The critical doses for complete amorphization of these phases are as low as <0.1 displacement per atoms (dpa) or 10^8 Gy in ionization energy deposition (a dose equivalent to that expected in a zeolite with 10 wt.% loading of ^{137}Cs in 400 years). Amorphization may be preceded or accompanied with dehydration, layer spacing reduction and gas bubble formation which may cause significant volume swelling. The critical radiation dose for amorphization or bubble formation in zeolites strongly depends on the size of channels available in the structure for gas release. In the case of zeolites, CST and some layer silicates, radiation effects are significantly enhanced at higher temperatures. Our experiments have shown that amorphization or even partial amorphization will cause a dramatic reduction (up to 95%) in ion exchange and sorption/desorption capacities for radionuclides, such as Cs and Sr. Because the near-field or chemical processing materials (e.g., zeolites

or CST) will receive a substantial radiation dose after they have incorporated radionuclides, our results suggest that radiation effects may, in some cases, retard the release rate of sorbed or ion-exchanged radionuclides. The results of these studies have a direct bearing on repository assessment (e.g., the extent to which zeolites can retard the release of radionuclides) and on the technologies used to process high-level liquid wastes (e.g., separation of ^{137}Cs from HLW using CST at the Savannah River Site).

Planned Activities

A systematic study on the changes in microstructure and ion exchange capacity of zeolite-NaY after proton beam irradiation is underway and will be completed by the extended ending date of the project. Also, analyses of recently acquired data from clays and CST will also be completed during the next three months. A final report of the project will be submitted within 90 days of the extended ending date of the project.

Information Access

(A) Web Site: http://relw.engin.umich.edu
(B) Publications Generated under the Project:

1. L.M. Wang, S.X. Wang, W.L. Gong and R.C. Ewing, "Temperature dependence of Kr ion-induced amorphization of mica minerals", Nuclear Instruments and Methods in Physics Research B 141 (1998) 501-508.
2. L.M. Wang, "Application of advanced transmission electron microscopy techniques in the study of radiation effects in insulators", Nuclear Instruments and Methods in Physics Research B 141 (1998) 312-325.
3. L.M. Wang, S.X. Wang and R.C. Ewing, "Radiation effects in zeolite: Relevance to near-field containment", Proceedings of the 9th Annual International High-Level Radioactive Waste Management Conference (American Nuclear Society, Las Vegas, NV, May 11-14, 1998), pp. 772-774.
4. L.M. Wang and R.C. Ewing, "Transmission electron microscopy study of radiation effects in materials for nuclear waste disposal", Electron Microscopy 1998, Proceedings of the 14th International Congress on Electron Microscopy (Cancun, Mexico, Aug 31-Sept. 4, 1998), Edited by H.A. Calderón Benavides and M. José Yacamán, Vol. 2, 825-826.
5. S.X. Wang, L.M. Wang and R.C. Ewing, "Electron irradiation of zeolites", Materials Research Society Symposia Proceedings 540 (1999) 361-366.
6. B,X, Gu, S.X. Wang, L,M. Wang, and R.C. Ewing, "Radiation and thermal effects on the structure and ion-exchange/ retention capacity of zeolites", Proceedings of the International Conference on the Future Nuclear Systems—Global'99 (American Nuclear Society, Jackson Hole, Wyoming, August 29-September 3, 1999).
7. B.X. Gu, L.M. Wang and R.C. Ewing, "The effect of amorphization on the Cs ion exchange and retention capacity of zeolite-NaY", Journal of Nuclear Materials 278 (2000) 64-72.
8. S.X. Wang, L.M. Wang and R.C. Ewing, "Electron and ion irradiation of zeolites", Journal of Nuclear Materials 278 (2000), in press.
9. Binxi Gu, Lumin Wang, Phil A. Simpson, Leah D. Minc and R.C. Ewing, "Radiation and thermal effects in zeolite-NaY", in: Scientific Basis for Nuclear Waste Management XXIII, R.W. Smith and D.W. Shoesmith eds. (Material Research Society, Warrendale, PA, 2000), in press.
10. L.M. Wang, B.X. Gu, S.X. Wang and R.C. Ewing, "Radiation effects on materials in the near-field of a nuclear waste repository", Proceedings of the 24th International Symposium on the Scientific Basis for Nuclear Waste Management, submitted.
11. B.X. Gu, S.X. Wang, L.M. Wang and R.C. Ewing, "The effetcs of proton beam irradiation on the Cs ion exchange capacity of zeolite-NaY", Journal of Nuclear Materials, to be submitted.

Analysis of Surface Leaching Processes in Vitrified High-Level Nuclear Wastes Using In-situ Raman Imaging and Atomistic Modeling

Project ID: 54982

Joseph H. Simmons, University of Florida

David E. Clark, University of Florida

Research Objective

The work was directed toward the investigation of quantitative remote analysis of the leaching process in glasses, using non-destructive optical methods for evaluating changes taking place on the sample surface.

Research Progress and Implications

After three years of research on this grant, we have examined the feasibility of various surface optical techniques for composition analysis, including Raman and reflection IR spectroscopies. Our results have demonstrated that reflection FTIR analysis can be used for determining the surface composition changes of a glass undergoing corrosion. The results show that glass surface composition during leaching can be measured *quantitatively*. The method uses ergodic analysis of dielectric constants corresponding to identified phonon resonances on the glass surface to determine changes in the glass surface composition with leaching. The process is currently applicable to silicate glasses.

The new methodology developed changes accepted wisdom and has revealed serious inaccuracies in canned software programs available with current instrumentations and previuosly published analyses of IR leaching studies. Since the method is adaptable to fiber optics transmission of the optical signals, it is useable in the storage vaults for continued monitoring of the waste glasses, and it can be used with radioactive materials with little personnel and equipment exposure. Remote sensing of the glass surface composition during storage or in a hot cell provides an invaluable tool for the examination of leaching processes in radioactive materials, and for in-situ tests in the nuclear waste repositories without human intervention.

Development of this program has required the derivation of the Kramers-Kronig transform to a Gaussian function. The analytical and derived equations have been converted into a simple software program which will be made available for analysis of reflection FTIR data.

Ongoing research includes the development of a user-friendly interface for the fitting program, the development of standard characteristics (peak position and peak width) for the IR bands of known molecular complexes and application of the analysis method to complex glasses of the type considered for waste vitrification. The method can be used in-situ and can be adapted to various flow tests proposed for support of the development of ground transport models.

Planned Activities

These efforts will not be covered by the grant period

(1) Development of methodology for using IR transmitting optical fibers for remote applications,
(2) Application of this approach to leaching studies on phase separated and crystallized glasses,
(3) Application of leaching studies to radioactive samples,
(4) Studies of the development of UV Raman facilities for conducting tests of submerged samples.

(5) Interaction with Tank Focus Team members to transfer the technology and developed programs to actual vitrified waste studies.

Publications

Steven A. MacDonald, Craig R. Schardt, David J. Masiello, and Joseph H. Simmons, "Dispersion Analysis of FTIR Reflection Measurements in Silicate Glasses," Journal of Non-Crystalline Solids, accepted for publication.

D. J. Masiello, S. A. MacDonald, C. R. Schardt, J. H. Simmons and S. A. McCullough, "Dispersion Functions for Optical Spectroscopy," Amer. J. Physics, submitted.

Awards

David Masiello, Undergraduate Scholar's Best Paper Award, University of Florida, 1999.

New Silicotitanate Waste Forms: Development and Characterization

Project ID: 60345

Dr. Mari Lou Balmer, Pacific Northwest National Laboratory

Dr. Tina Nenoff, Sandia National Laboratories
Prof. Alexandra Navrotsky, University of California-Davis
Dr. Yali Su, Pacific Northwest National Laboratory

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 Cs and Sr 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, to minimize the risk of contamination to the environment during CST processing, and to provide DOE with technical alternatives for CST disposal. The technical objectives of the proposed work are to fully characterize the phase relationships, structures and thermodynamic and kinetic stabilities of crystalline silicotitanate waste forms and to 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 resulting from heat treated CST and from model 3-component systems, and 3) investigate thermodynamic stabilities of compounds related to the ion-exchanged CST and the thermally converted oxides. Leach tests have shown that durabilities of waste forms resulting from a simple heat treatment of the Cs-loaded CST *with no additives* in the range of 800-1000°C were orders of magnitude higher than that of baseline borosilicate glass. Cs volatilization was found to be approximately 3 wt% at temperatures as high as 1000°C. In addition heat treatment reduces waste volume by approximately 40% and simultaneously coarsens fines, thus reducing inhalation risks. Heat treatments above 800°C completely removes molecular water and hydroxyl groups so that the possibility of radiolytic hydrogen production during storage is eliminated.

A number of new phases appear when IE-911 is heat-treated. Nuclear magnetic resonance (NMR), x-ray diffraction (XRD), and transmission electron microscopy (TEM) results indicate that major phases in thermally converted CST are $Cs_2X1Si_3O_9$, $Na(TiX2)O_3$, and $Na_2Ti_6O_{13}$ (where X1 and X2 are proprietary components of the ion exchanger). 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 high aqueous durability of $Cs_2X1Si_3O_9$ can be explained by its small channel size (smaller than a Cs ion) which precludes facile migration of Cs. 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 1.1×10^{22} e/cm^2.

A second new phase discovered by TEM (Na, Ti, X2, oxide) has a structure similar to the perovskite $NaX2O_3$. In order to determine the extent of titanium substitution in this mixed phase, a series of compounds with up to 20% Ti substitution were synthesized using a sol gel technique. A systematic shift of the lattice parameter as a function of Ti substitution has been observed. Comparison of the heat-treated IE-911 with the synthesized compounds revealed that this phase in IE-911 has 15% Ti substitution in the lattice.

In the course of Na_2O-TiO_2 hydrothermal phase searches, researchers at SNL discovered a novel Na/Ti/M/O class of molecular sieves. These phases show high selectivity for divalent cations over monovalent cations, which is a useful characteristic for numerous applications including extraction of ^{90}Sr or Pb from mixed wastes. Additionally, direct thermal conversion of these ion exchangers produces a perovskite, which is a durable phase. Structural characterization of these phases is currently underway.

Phase equilibria and single crystal growth experiments on the three component Cs_2O-TiO_2-SiO_2 system have revealed several new compounds. SNL-A and SNL-B were synthesized hydrothermally at SNL, $Cs_2TiSi_6O_{15}$ and $CsTiSi_2O_{6.5}$ by sol-gel methods at PNNL. A complete solid substitution series of $Cs_2TiSi_6O_{6.5}$ and $CsAlSi_2O_6$ has been synthesized. Substitution of Ti for Al in pollucite results in stabilization of the cubic structure at low temperatures (to 100K). The standard molar enthalpies of formation from Ti-substituted pollucites with the composition $CsTi_xAl_{1-x}Si_2O_{6+0.5x}$ have been determined at UC Davis by solution-drop calorimetry. As Ti^{4+} substitutes for Al^{3+} in pollucites, the enthalpies of formation become more endothermic and show exothermic mixing within the composition ranging from x = 0.3 to 1. This non-ideal mixing behavior is consistent with the trend seen in the 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+}. The enthalpies of formation for pharmacosiderite analogues with the composition $(K_{1-x}Cs_x)_3Ti_4Si_3O_{15}(OH)\cdot 4H_2O$ become more exothermic as Cs/(Cs+K) increases. This result indicates that the incorporation of Cs in these phases is thermodynamically favorable, although kinetic factors may play a role as well.

Planned Activities

The stability of Cs-containing compounds during their radioactive decay (to ^{137}Barium) is of concern. Solid solutions such as (Ba, Cs) $X1Si_3O_9$ will be synthesized and the thermodynamic stability, chemical durability, crystal structure, and local Cs environment will be probed. The heat of formation of these and the other representative ternary and quaternary compounds will be measured.

Information Access

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Chemical Decomposition of High-Level Nuclear Waste Storage/Disposal Glasses Under Irradiation

Project ID: 55188

Dr. David L. Griscom, U.S. Department of the Navy

Research Objective

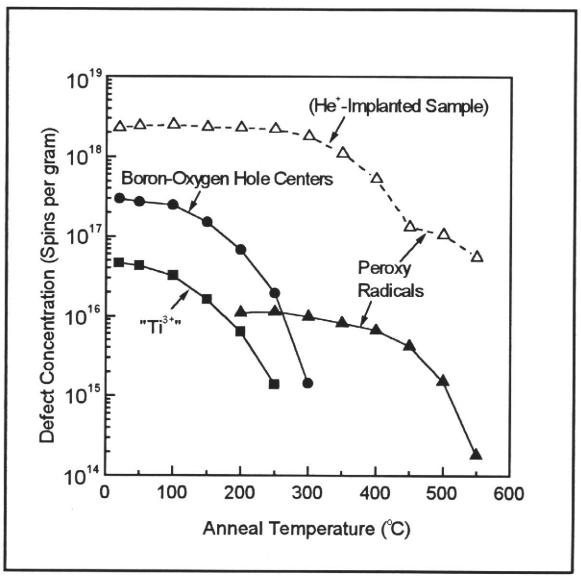
The objective of this project is to employ the technique of electron spin resonance (ESR), in conjunction with other experimental methods, to study radiation-induced decomposition of vitreous compositions proposed for immobilization/disposal of high-level nuclear wastes (HLW) or excess weapons plutonium. ESR is capable of identifying, even at the parts-per-million level, displaced atoms, ruptured bonds, and free radicals created by radiation in such glassy forms. For example, one of the scientific goals is to search for ESR-detectable superoxide (O_2^-) and ozonide (O_3^-) ions, which could be precursors of radiation-induced oxygen gas bubbles reported by other investigators via the disproportionation reaction, $2O_2^- \leftrightarrows O_2^{2-} + O_2$. The fundamental understandings obtained in this study will enable reliable predictions of the long-term effects of α and β decays of the immobilized radionuclides on the chemical integrity of HLW glasses.

Research Progress and Implications

This report summarizes the results of a 30-month effort performed under a 3-year research award. Four categories of materials were studied: (A) several actual and proposed HLW glass compositions fabricated at Savannah River Technology Center (SRTC), (B) several high-iron phosphate glasses fabricated at the University of Missouri-Rolla (UMR), (C) an iron-free boro-aluminosilicate model HLW glass subjected to γ rays (to simulate β-decay effects) and to implantation by 160-keV He^+ ions (to simulate α-decay damage), and (D) well-dated geological glasses damaged by α decays of trace amounts of contained ^{238}U and ^{232}Th over a period of 65 million years. Among materials A were two samples of Defense Waste Processing Facility (DWPF) borosilicate glasses modeling compositions currently being used to vitrify HLW at SRTC. The ESR spectra recorded for the unirradiated DWPF-glass simulants were attributable to Fe^{3+} ions and/or precipitated ferrites. The sole effect of a 30-MGy γ irradiation (1 Gy = 100 rad) was to change the Fe^{3+} concentration of these glasses by a statistically insignificant factor (0.987 ± 0.050). No induced defect centers were measurable by ESR, possibly due to a suppression effect of the Fe^{3+} ions. (N.B. The presence or absence of radiolytic O_2 cannot be directly determined by ESR.)

Another category-A material, an iron phosphate glass containing Li_2O and CeO_2, displayed a much larger γ-radiation ESR response than did the DWPF glass. Specifically, ~$2x10^{18}$ radiolytic superoxide ions (O_2^-) ions per gram were identified in this glass by ESR [1]. Since high-iron phosphate glasses in general (composition range ~$0.2<[Fe]/[P]<0.67$) have displayed many properties favorable for vitrification of phosphate-rich high-level wastes such as are present at the Hanford site [2], the first 15 months of the project were devoted to fundamental studies of (A) the SRTC lithium-cerium-iron-phosphate and (B) various UMR iron-phosphate glasses. The results of ESR, Mössbauer, thermal analysis, and gas-evolution studies carried out in informal collaboration with the UMR and Toyo University (Japan) are reported in [1]. The ESR results have revealed the unirradiated glasses to possess unusual long-range magnetic structure, which is qualitatively different than that of the crystallized materials. This finding, in conjunction with the other types of measurements mentioned, led to the tentative proposal that peroxide ions (O_2^{2-}) may have been incorporated in the *as-prepared glasses*. Whether or not this model proves correct, the present work has inspired a planned polarized-neutron-diffraction study [3] to better elucidate the topology of the glass network.

More recently, samples (C) were examined in detail. ESR spectra were recorded before and after irradiation and after 10-minute postirradiation isochronal anneals. The most numerous paramagnetic states in the unannealed samples following γ irradiation were boron-oxygen trapped-hole centers and Ti^{3+} trapped-electron centers and, following He^{+} implantation, peroxy radicals (PORs: O_2^- ions bonded into the glass network). Annealing the γ-irradiated samples above 300°C caused recombination of the trapped electrons and holes, revealing an underlying POR spectrum which annealed in stages at ~400 and 550°C, similar to the annealing of PORs in the He^{+}-implanted sample (see figure). Normalized to the amount of ionizing energy deposited, the initial POR concentration in the He^{+}-implanted sample was ~100 times that in the γ-irradiated sample. It is thus evident that the PORs induced by He^{+} implantation result from displacements of oxygens in elastic collision cascades. The absence of trapped electrons and holes in the implanted samples is ascribed to annealing during irradiation associated with the fraction of the implantation energy deposited as heat. One of the fundamental defects to be expected in HLW glasses containing α-particle emitters is therefore the POR [4]. 65-million-year-old glasses displayed narrow ESR signals, possibly due to O_2^- ions, which may have resulted from α decays of contained radionuclides. These geological glasses provided anecdotal evidence for an influence of Fe^{3+}/Fe_{total} on the numbers of O_2^- ions observed. It is argued in [4] that the presence of several wt % Fe_2O_3 may suppress the formation of O_2^- ions without impeding production of neutral O_2 molecules. Since virtually all HLW streams contain iron oxides, this issue requires further clarification.



Planned Activities

Planned activities include ESR studies of seven different model HLW glasses, fabricated, γ-irradiated at four different temperatures, and provided by Pacific Northwest National Laboratory (PNNL). These samples include borosilicate glasses with differing iron contents and two iron phosphate glasses. PNNL will also supply three HLW glass simulants loaded with 1 wt% plutonium which were fabricated 15 years ago. The PNNL glasses containing ^{238}Pu (half life 87.7 years) will be shipped as soon as the appropriate site license is issued by the NRC to the Naval Research Laboratory. These samples will emulate the combined effects of α-particle and α-recoil damage occurring in actual HLW glasses over periods of 10^3 to 10^6 years or in ^{239}Pu-containing glasses after 4,000 years. Not only will this emulation be superior to simulation by He-ion implantation but it will also yield a 1000-fold improvement in ESR signal-to-noise ratios due to full volumetric irradiation of the samples. Searches for radiolytic O_2^- and O_3^- ions will be continued, particularly in relation to the possible influence of

iron content. Due to the delayed arrival of these samples, a no-cost extension will be requested to complete this work.

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Microstructural Properties of High Level Waste Concentrates and Gels with Raman and Infrared Spectroscopies

Project ID: 54773

Dr. Stephen F. Agnew, Los Alamos National Laboratory

Dr. Clifford T. Johnston, Purdue University

Project Objectives

year 1: Initial efforts will focus on developing an understanding of the aluminate chemistry in concentrates. FTIR, Raman, and ^{27}Al NMR experiments will be undertaken with heats of gelation measured by DSC and related to aluminate composition and speciation. The necessary optics for a Raman mircroprobe to the JY U1000 Raman spectrometer will be purchased and interfaced. Measurements of viscosity, density, and surface tension for each gel prepared will be conducted and related to the vibrational measurements with these macroscopic characteristics. Measurements of water activity will be initiated and correlated with spectroscopic observables.

year 2: Raman spectroscopic measurements on bulk slurries/gels will be completed, and Raman microscopy experiments initiated. The Raman microscopy will require development and adaptation of an existing microscope to the JY U1000 spectrometer. Infrared spectral features will be correlated to water activity to evaluate the presence of liquid voids in gels and slurries, and evaluate the effect of organic salts on water activity. Heats of gelation will be measured for the concentrates and correlated to the micro-Raman measurements and liquid void fraction.

year 3: Final vibrational spectroscopic studies will be completed. Data will be collated and used to refine the microscopic understanding of the behavior of waste concentrates. This information will be utilized to formulate an understanding in order to make predictions of aluminate waste behavior as a function of temperature and water content. The third year's efforts will be refined to further the understanding of these materials. Specific objectives include: (1) a spectroscopically based determination of aluminate monomer/dimer equilibrium constant , (2) completion of aluminate phase diagram, (3) precise determination of the role of water activity and free vs. bound water in aluminate speciation, (4) identification and characterization of key aluminate dimeric/oligomeric species via their vibrational spectroscopic signatures, and (5) characterization of alumino-carbonate species in solution derived from incorporation of atmospheric CO_2 into aluminate slurries.

Nearly half of the high level radioactive waste stored at Hanford is composed of highly alkaline concentrates referred to as either salt cakes or Double-Shell Slurry (DSS), depending on their compositions and processing histories. The major components of these concentrates are water, sodium hydroxide, and sodium salts of nitrate, nitrite, aluminate, carbonate, phosphate, and sulfate. In addition, there are varying amounts of assorted organic salts such as EDTA, glycolate, and citrate. Although measurements of the bulk properties of these wastes (e.g. viscosity, gel point, density) have been reported, little is known about how the macroscopic characteristics are related to the microscopic physico-chemical properties. Viscosity, solids volume percent, and gas retention can dramatically change with relatively small changes in composition and temperature. Furthermore, these same properties are important in determining safe storage conditions as well as in planning retrieval, pretreatment, and disposal of the wastes. The focus of this effort will be on aluminate chemistry since large inventories of waste with aluminum are located at Hanford and Savannah River and little is known about the microstructure of these complex mixtures.

The goal of the proposed work is to relate molecular scale information to macroscopic behavior. The approach will utilize FTIR, Raman, and ^{27}Al NMR spectroscopies along with thermo-physical

heats of gelation to relate the physico-chemical properties of these concentrates to macroscopic behavior. The primary experimental approach will include the following:

- Water vapor pressure measurements for concentrates to determine water activity as a function of composition and temperature.
- FTIR, Raman, and ^{27}Al-NMR spectroscopies to determine the form and solubility of aluminate in caustic slurries.
- Micro-Raman spectroscopy to identify and quantify phases of each species for a variety of concentrates.
- Measurements of the heat of gelation and its dependence on water activity, presence of organics, and other properties.
- Spectroscopic tools to assess the influence of organic salts on microstructural properties of slurries.

Research Progress and Implications

The major focus of this research effort has been to explore the chemical mechanisms associated with gels and slurries and relate these to the observed general behavior. Experimentally, samples of known composition have been prepared that simulate the dominant components of Hanford caustic aluminates. The chemical components are known and the activity of water is controlled.

Raman spectroscopic studies have been utilized to probe the speciation of the aluminate (monomer vs. dimer) and the identification of the solid phases present. Raman bands for aluminate indicate formation of dimers and oligomers in solution. These Raman data provide new insight into the structure of caustic aluminate solutions.

Infrared spectroscopy has also been used to monitor water activity. Water in these systems can be free, coordinated to Na^+ and $Al(OH)_4^-$ monomer ions, or structurally associated with monosodium or trisodium aluminate solids. The data indicate that the activity of water defines the stability of solid phases and provides information about precursors to precipitation.

^{27}Al-NMR studies have been pursued to study the coordination of Al in these solutions. The NMR studies reveal a tetrahedral coordination of aluminum. The ^{27}Al-NMR experiments do not effectively show the formation of dimeric or oligomeric coordinated aluminum environments. Vibrational spectroscopic methods do, however, as noted above, discriminate between aluminate monomers and dimers/oligomers. Moreover, Raman depolarization ratio studies reveal subtle differences in dimer and oligomer properties in response to changing mixture compositions.

Connecting these data to actual tank waste is best accomplished using a phase diagram. Evaporation lines can be used to predict which solids will precipitate. Depending upon the location within the phase diagram, dilution of supernatant will result in precipitation. The current data are being mapped into a phase diagram and experiments are being pursued to complete key regions of the diagram that heretofore have not been explored.

Planned Activities

We are on schedule to complete the scope of work noted above for the third year with the current funding level. Data will be collected to complete publication of the results in a refereed journal (project PI and the university collaborators already have created a rough draft of a paper to be submitted to ‘Environmental Science and Technology’) and final report.

Considering the long-term significance of this research, the future direction of this research effort will be explored within the last half-year of this work and a proposal formulated.

Ion-Exchange Processes and Mechanisms in Glasses

Project ID: 60362

B. Peter McGrail, Pacific Northwest National Laboratory

Research Objective

Current 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 [1]. 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 [1]. 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 constant pH=8. The Series I glasses showed increasing Na 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 compared to 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 (^{a}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; Na-exchange rates were found to decrease with 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) [2]. The magnitude of Na depletion decreased with increasing Al_2O_3 content in the glasses. Na-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 spectroscopy (MAS-NMR) was performed on the Series I and Series II glasses. 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 Al 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 XANES and 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 Na atoms. In summary, the EXAFS measurements show greater order and tighter bonding of Na in the glass structure as Al_2O_3 is added, and this is consistent with the lower rate of Na ion exchange observed for these glasses.

Planned Activities

1. Complete glass-water reaction experiments 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).
2. 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.

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Mechanism of Pitting Corrosion Prevention by Nitrite in Carbon Steel Exposed to Dilute Salt Solutions

Project ID: 60401

Dr. Philip E. Zapp, Westinghouse Savannah River Company

Dr. John W. Van Zee, University of South Carolina

Research Objective

The overall goal of this project is to develop a fundamental understanding of the role of nitrite in preventing the breakdown of protective oxide(s) on carbon steel and the onset of pitting. Pitting corrosion of carbon steel exposed to dilute alkaline salt solutions can be induced by nitrate, sulfate, and chloride ions and is prevented by sufficient concentration of nitrite. A significant example of this material/electrolyte system is the storage and processing of DOE's high-level radioactive liquid waste in carbon steel tanks. Added nitrite in the waste has a considerable downstream impact on the immobilization of the waste in a stable glass form. Waste tank integrity and glass production efficiency may benefit from the fundamental understanding of nitrite's role in preventing pitting.

Research Progress and Implications

This report summarizes progress for the last 12 months. It accounts for approximately eighteen months of effort in this three-year EMSP project. This report adds to the report submitted last year (June 1998) which described progress after approximately six months of the project. The planned activities of the project are listed at the end of the report. We have updated the completion dates and projections to reflect the current status of the project. During the last year we experienced a four-month delay on the spectroscopic studies task when the circuit board on the FT-IR instrument overheated and required repair and re-calibration. At this time we expect to complete all of the tasks of the project on time despite this instrument failure.

The experimental and theoretical work has continued to focus on the electrochemical behavior of carbon steel in simplified non-radioactive solutions that simulate complex dilute radioactive waste solutions. These solutions contain corrosion-inducing species such as nitrate and chloride and the corrosion-inhibiting nitrite at moderately alkaline pHs. We are interested in three critical aspects of the electrochemical behavior. One aspect is that of the open-circuit potential of the steel specimen at equilibrium and we are interested in how it changes as a function of inhibitors in the experimental electrolyte. The other two aspects include measures of the steel's passivity and passivity breakdown.

We have published two refereed papers in conference proceedings (1,2) that describe measurements of these aspects as a function of inhibitor concentration and electrolyte concentration. We have completed the design of combined spectroscopic-electrochemical cells for the purpose of studying the surface species as a function of applied potential and electrolyte concentration. We have begun the FT-IR and FT-Raman experiments. We have developed a model to describe the data on the open-circuit potential and the current-potential relationship prior to pit formation (3). This model will be presented in November and a paper will be submitted prior to that conference. We have started a second model to describe the electrochemistry that occurs in a pit as a function of electrolyte composition and concentration.

Electrochemical Studies

The electrochemical behavior is evaluated by the cyclic potentiodynamic polarization (CPP) technique. The technique involves the measurement of the electric current (i.e., the electrochemical reaction

rate) in response to a voltage, or potential, applied to the test specimen. The technique can reveal the susceptibility of an alloy to pitting corrosion, which initiates upon breakdown of a passive film on the metal specimen. In a CPP scan, passivity manifests itself through a range of applied potential in which the resulting passive current (density) is unvarying. Passivity breakdown is expressed experimentally as the potential at which the current increases abruptly from a relatively low, potential-*independent* value.

Cyclic potentiodynamic polarization scans were conducted on specimens of ASTM A537 carbon steel, the waste tank material of construction. In the present experiments, the potential was scanned from near the open-circuit potential to about +1 volt with respect to a saturated calomel reference electrode (1V SCE) and then returned to near the open-circuit value. The scan rate was 0.5 mV/sec, which is a reasonable balance between approximating steady-state conditions and acquiring data efficiently. Test solutions were mixed from reagent grade chemicals and distilled water. The solutions contained various nitrate and chloride concentrations. The initial pH of the solutions was 9.7 (established by a bicarbonate-carbonate equilibrium), and the test temperature was 40°C.

Initial experiments demonstrate significant differences in the steel's behavior in nitrate versus chloride solutions. Chloride is the classic initiating ion of pitting corrosion. With increasing chloride concentration in the range 0.01 to 0.3 M, the breakdown potential decreases from a value above the transpassive transition (~ 750 mV SCE) to a value below the open-circuit potential (open-circuit potentials range from -500 to -100 mV SCE). Chloride-induced breakdown is mitigated by nitrite; and nitrite drives the breakdown potential higher. Nitrate has been shown to induce pits in carbon steel, and such pitting can also be mitigated by nitrite. In fact the action of nitrite is empirically the same for nitrate and chloride. However, in the present experiments increasing nitrate concentrations do not result in the observation of a breakdown potential. CPP scans in solutions with a nitrate concentration of as high as 2.2 M continue to show a transpassive transition at about 750 mV SCE. The corrosivity of nitrate toward carbon steel *is revealed* in an increase in the passive current density. These results have been presented as shown in Refs. 1 and 2. We expect to perform additional experiments to verify and test hypotheses formulated during the development of the models and during the analysis of the spectroscopic studies.

Spectroscopic Studies

In addition to the potentiodynamic polarization scans, spectroscopic studies have been started. The goal of these studies is to investigate the oxide film and its response to changes in the concentration of corrosive and protective species with *in-situ* vibrational spectroscopy. A specially designed cell has been constructed to allow for combined Electrochemical Impedance Spectroscopy and FTIR or FT Raman measurements. These EIS/FTIR and EIS/FT Raman cells will be used to determine if surface enhanced signals can be observed. Raman/EIS cells are being tested using a number of optical configurations.

One of these designs will be used to test the cell optics and Raman sensitivities and it will incorporate two glass plates. A thin metallic film will be deposited on the inner surface of one plate. The space between the plates will contain the test solution. Counter and reference electrodes have been installed. The cell can then be positioned in the Raman spectrometer in two orientations: (1) the exciting beam passes through the unmetallized plate and solution before striking the metal film; and (2) the beam enters through the back of the metallized plate and strikes the film from the rear. The evanescent Raman from this orientation will minimize optical sampling of the solution.

Another design studied this year includes the use of ASTM A537 carbon steel as the back plate with one of the glass plates as the front plate. We are working on minimizing the signal loss through the solution with this configuration. The advantage to this design is the ability to polish the surface of the cell to the same roughness as the coupons in the electrochemical studies. We will be studying techniques to initiate the pit at a specific point to facilitate the observations in a pit. Results of these studies were delayed during the last year due to a failure of a circuit board and a tuning laser on the FT-IR portion of the FT-Raman. The instrument has been repaired and re-calibrated and preliminary data has been obtained. The spectroscopic studies will be a major focus of the work during the next year.

Analysis and Modeling

The analysis of the passivation/activation phenomena has been aided by a fundamental understanding of the solution chemistry. Studies of the interaction of nitrate and nitrite seem to indicate that the redox reactions shown by reactions 1-5 below are involved. As a first step in the analysis of the solution effects, the effect of ionic strength on the equilibrium and solubility products for the Pourbaix diagram has been calculated using equation 6. Here the dilute solution equilibrium constant, $K_{eq.}$ and the actual equilibrium constant Q_{eq} are related to the ionic strength, ***I***, the molality of the dominant species. Reference 1 presents the effects of ionic strength on the Pourbaix diagram and showed that the regions of film formation and dissolution changed significantly with concentration of simulant at the pH of the experiments. Future work will involve the effect of temperature on the equilibrium solubility products, the hydrolysis reactions, and the exchange current densities for film breakdown. We plan to study theoretically the adsorption characteristics of chloride, nitrate, and nitrite as a function of temperature and ionic strength and to compare these with the data from the spectroscopic studies.

	U (V)	
$1/2NO_3^- + 1/2H_2O + e \rightarrow 1/2NO_2^- + OH^-$	0.011	**(1)**
$1/6NO_2^- + 5/6H_2O + e^- \rightarrow 1/6NH_3 + 7/6OH^-$	-0.165	**(2)**
$1/3NO_2^- + 2/3H_2O + e^- \rightarrow 1/6N_2 + 4/3OH^-$	0.406	**(3)**
$1/2NO_2^- + 3/4H_2O + e^- \rightarrow 1/4N_2O + 3/2OH^-$	0.151	**(4)**
$H_2O + e^- \rightarrow 1/2H_2 + OH^-$	-0.828	**(5)**

$$\log Q_{eq} = \log K_{eq} + \frac{aI^{1/2}}{1 + I^{1/2}} + b_{eq} m_2 \qquad \textbf{(6)}$$

We have also developed a model to describe the data on the open-circuit potential and the current-potential relationship prior to pit formation (3). The model for the initiation of a pit in iron is developed by using Figure 1. The mass fluxes include diffusion, migration, and convection in the two-region, three-boundary condition problem. Six species plus the potential are used as dependent variables and two electrode reactions were considered to take place on steel surface. One is iron electrode reaction; the other is reversible reduction of nitrate to nitrite.

The competition of nitrite oxidation and iron oxidation can partially explain the inhibition of nitrite to iron corrosion. Predictions have been prepared for the concentration profiles through the passive film and diffusion layer, for the solution potential distribution, and for the relationship between the steel's potential and the overall current density. The model results are being used to test hypotheses and to suggest reaction mechanisms for the passivation behavior by comparing the V-I predictions with experimental data for different ratios of NO_2^-/NO_3 concentrations as shown in Figures 2 and 3. This model will be presented in November and a paper will be submitted prior to that conference. We have started a second model to describe the electrochemistry that occurs in a pit as a function of electrolyte composition and concentration according to the schematic of Figure 4.

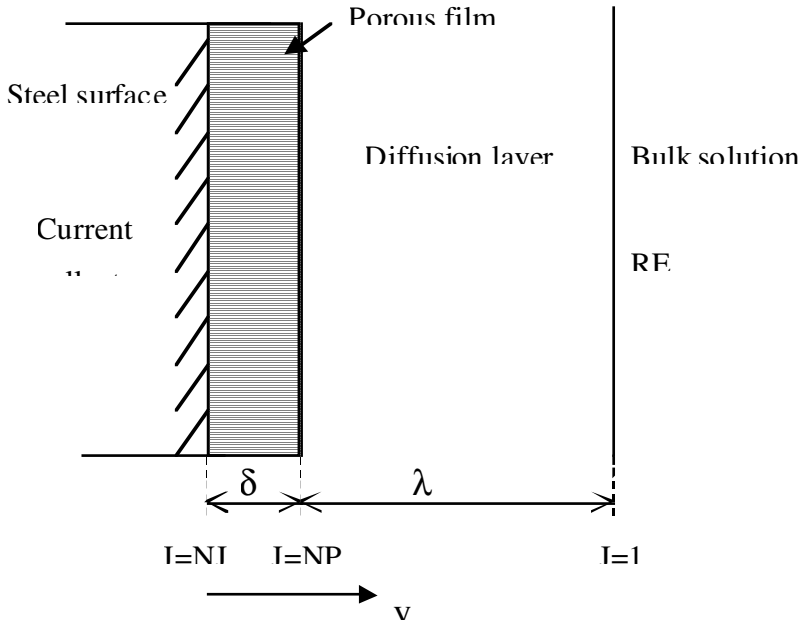

Figure 1. Schematic diagram for the first model.

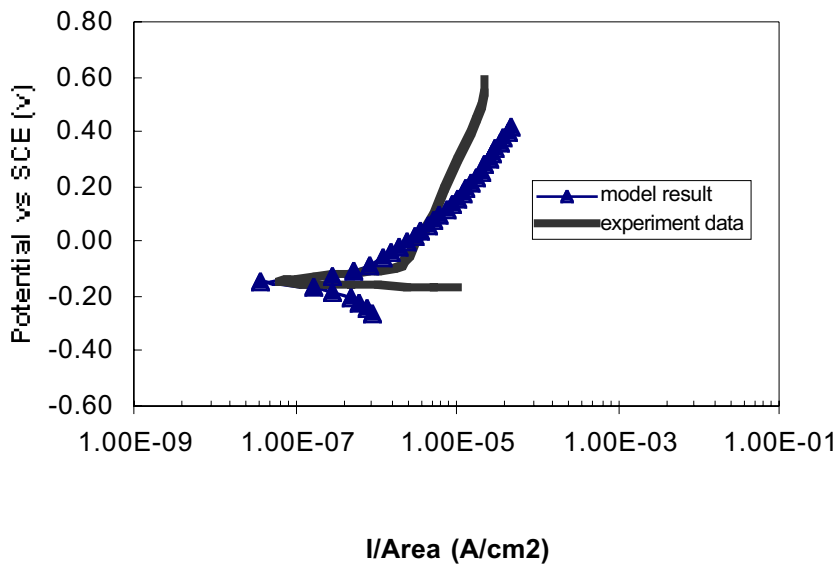

Figure 2.Comparison of experiment data and model predictions. The experiment data comes from cyclic potentiodynamic polarization scans at 0.02M nitrate and 0.11M nitrite as shown in Ref. 2.

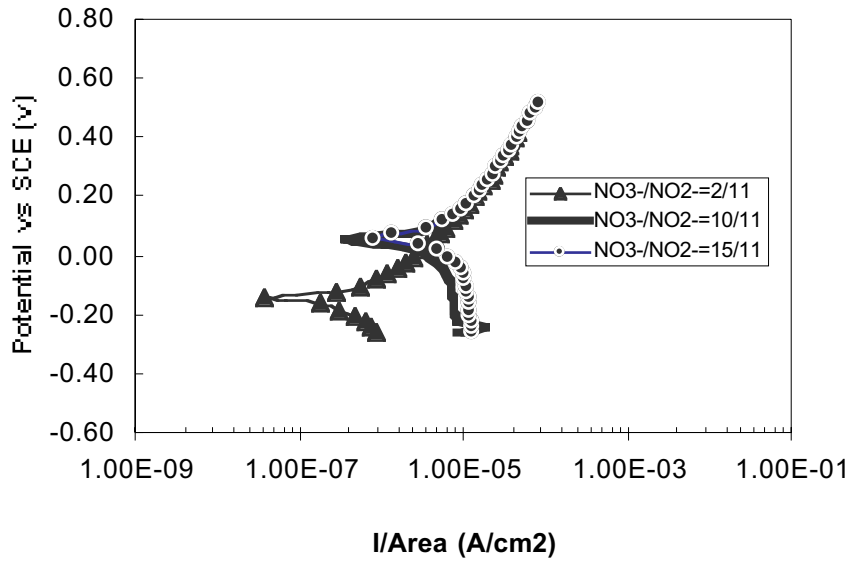

Figure 3. Predictions of the effect of the nitrate/nitrite ratio on the potential-current relationship.

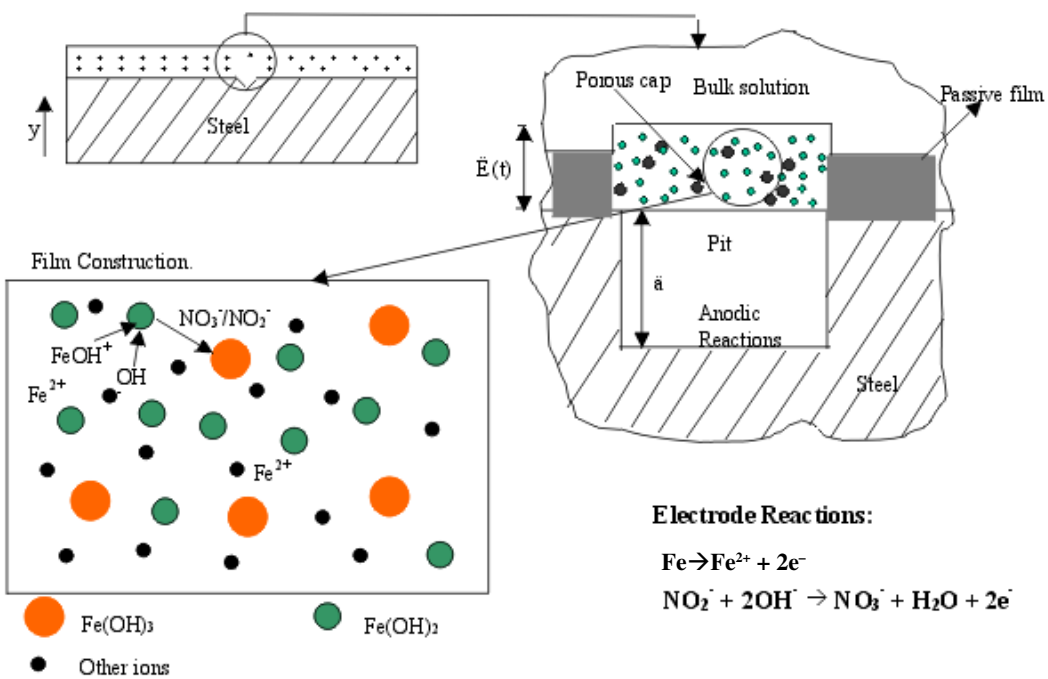

Figure 4. Schematic for Pit Model.

Planned Activities

Activity	*Completion*
1. Perform potentiodynamic and potentiostatic scans to evaluate the differences in the chloride and nitrate effects on the breakdown potential and passive current density.	12/98
2. Spectroscopic studies to design & fabricate EIS/FTIR and EIS/FT Raman cells	12/98
3. Perform measurements to check for surface enhancement and study the effect of the exciting beam passing through the solution before striking the metal film and the effect of the exciting beam passing through the back of the metallized plate and striking the film from the rear.	5/00
4. Mathematical model of pitting phenomena	9/00

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The Influence of Radiation and Multivalent Cation Additions on Phase Separation and Crystallization of Glass

Project ID: 59827

Dr. Michael C. Weinberg, University of Arizona

Research Objectives

The major objectives of this proposed investigation are as follows:

(1) To investigate the influence of multivalent cations on the thermodynamics and kinetics of phase separation and crystallization in simple model glasses. (2) To study the influence of a and b particle, heavy ion bombardment and γ irradiation on phase separation and crystallization in simple model glasses. (3) To examine the structural changes produced by radiation just prior to the onset of phase separation and/or crystallization. (4) To develop models to explain the observed effects of multivalent cations and radiation on phase separation and crystallization. (5) To utilize the results of these experimental and modeling studies to provide guidelines for the allowed range of composition choices and processing conditions in order to avoid the formation of unwanted phases in nuclear waste disposal glasses.

Research Progress and Implications

We have been pursuing research activities in three areas: (1) assessment of the influence of γ radiation on phase transformation behavior, (2) measurement of valence state ratios of iron in glass, and 3) study of the effect of iron redox ratio on phase separation behavior in a glass.

For topic (1), we have selected glasses in three composition families(Na_2O-SiO_2, Li_2O-SiO_2, and K2O-SiO_2, called NS, LS, and KS) for investigation, and glasses of all of these compositions have been prepared and have been cut into one cm. cubes and have been inserted into the gamma ray pit at PNNL. The first glass system which is being investigated is the NS system. NS glasses show a region of immiscibility from about 0 - 20 mol % NS, and while NS_2 only exhibits surface crystallization, compositions in the vicinity of NS show both internal and surface crystallization. It is believed that radiation bombardment could qualitatively change the phase separation and crystallization behavior of these glasses. While a portion of the glasses have been undergoing radiation, the crystallization behavior of other NS glasses (which did not receive radiation) has been studied. We have determined the steady-state crystal nucleation rates of several NS compositions, and we have currently initiated an investigation of transient nucleation in one NS composition. We plan to compare the crystallization behavior of the irradiated glasses with those which do not receive radiation treatment.

Redox ratios have been determined using a colorimetric method, Mossbauer analysis, and optical absorption. Our work utilizing these methods is described below.

A UV/Vis Colorimetric method for determining Fe^{2+} as well as total iron was obtained from PNNL (Procedure number APSL-02). We have modified the PNNL procedure slightly. For the determination of total iron, the PNNL procedure suggests diluting a small amount of the Fe^{2+} sample by 100, then reducing the Fe^{3+} to Fe^{2+} by hydroquinone. This dilution step was suggested as the operating procedure was designed for rock or mineral samples that had a large amount of total iron, with a large amount of the iron in the ferric state. Diluting the samples was required in order to get the concentration of the iron ions to be low enough to obtain a solution that could be used in the spectrometer. For the glasses that we are using, the iron concentration is low enough that no dilution is necessary. We also have some glasses with very high Fe^{2+} concentrations, so dilution is an unnecessary step. We now take the Fe^{2+} solutions, and add hydroquinone directly (without dilution)

to determine the total iron level. This non-dilution technique has resulted in analyses which are much more reproducible and accurate, as any small errors in dilution has a large effect on the calculated redox ratio. This technique has been used successfully for 18.56 NS with up to 4 mol % FeO, 13 NS with up to 2 mol % FeO, and the 518 composition (5 Na_2O, 1 Fe_2O_3, 8 SiO_2)

Mossbauer analysis of 2 samples of the 518 glass with different oxidation levels and 2 samples of the 18.56 NS glass with two different oxidation levels has been completed at PNNL. The redox results are consistent with the modified UV/Vis Colorimetric procedure. We have prepared a number of thin glass samples for use in the UV/Vis/NIR Spectrometer for the determination of redox level. Initial results indicate that the absorption around 1120 nm is dependent on the iron redox ratio. We will be using the full range of glass compositions and oxidation states available to us to verify this technique for the determination of iron redox level. One other potential advantage to this technique is that the amount of water in the glass can be determined concurrently from the spectra.

The thermodynamics of phase separation in iron doped NS glasses has been studied as a function of Fe^{++}/Fe^{+++} (redox ratio) in the glasses. Binodal temperature measurements have been made for two compositions (18.56% N and 13% N) within the binodal which contain identical total iron concentrations but different redox ratios. For both compositions it is found that the addition of iron suppresses the immiscibility temperature. However, we observed that to within experimental error the immiscibility temperature is independent of redox ratio. This is a rather surprising result since arguments based on ionic field strength of cations would indicate a strong dependence of the binodal to the value of the redox ratio. Currently, we are seeking explanations for this unusual behavior.

Planned Activities

In the next year the following activities are planned:

(1) Prepare a manuscript describing our results on the influence of Fe^{++}/Fe^{+++} on the immiscibility temperature of glasses in the NS system. (2) Examine the crystallization behavior of the NS glasses which received g irradiation. (3) Perform structural studies and additional characterizations of the "unperturbed" glass compositions inserted into the gamma pit (to serve as baseline). (4) Complete our studies and prepare a manuscript on a comparison of experimental methods for obtaining iron redox ratio values in glass. (5) Examine the phase separation behavior of glasses in the KS and NS systems which have and have not been irradiated. (6) Examine metastable crystal phase formation in irradiated LS_2 glasses.

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Physical, Chemical and Structural Evolution of Zeolite-Containing Waste Forms Produced from Metakaolinite and Calcined HLW

Project ID: 65366

Dr. Michael Grutzeck, Pennsylvania State University

Dr. Carol M. Jantzen, Westinghouse Savannah River Company

Research Objectives

Natural and synthetic zeolites are extremely versatile materials. They can adsorb a variety of liquids and gasses, and also take part in cation exchange reactions. Zeolites are easy to synthesize from a wide variety of natural and man made materials. One combination of starting materials that exhibits a great deal of promise is a mixture of metakaolinite and/or Class F fly ash and concentrated sodium hydroxide solution.[1] Once these ingredients are mixed and cured at elevated temperatures, they react to form a hard, dense, ceramic-like material that contains significant amounts of crystalline tectosilicates (zeolites and feldspathoids).

Zeolites have the ability to sequester ions in lattice positions or within their networks of channels and voids. As such they are nearly perfect waste forms, the zeolites can host alkali, alkaline earth and a variety of higher valance cations. In addition to zeolites, it has been found that the zeolites are accompanied by an alkali aluminosilicate hydrate matrix that is a host, not only to the zeolites, but to residual amounts of insoluble hydroxide phases as well. A previous publication[2] has established the fact that a mixture of a calcined equivalent ICPP waste (sodium aluminate/hydroxide solution containing ~3:1 Na:Al) and fly ash and/or metakaolinite could be cured at various temperatures to produce a monolith containing Zeolite A (80°C) or Na-P1 plus hydroxysodalite (130°C) crystals dispersed in an alkali aluminosilicate hydrate matrix. Dissolution tests have shown these materials (so-called hydroceramics) to have superior retention for alkali, alkaline earth and heavy metal ions.

The zeolitization process is a simple one. Metakaolinite and/or Class F fly ash is mixed with a caustic sodium-bearing calcine and enough water to make a thick paste. The paste is transferred to a metal canister and "soaked" for a few hours at 70-80°C prior to steam autoclaving the sample at ~200°C for 6-8 hours. The waste form produced in this fashion could be a viable alternative for fixation of low activity waste (LAW) calcines. Our objective is to adapt this technology for use in site remediation and clean up of caustic waste solutions now in storage in tanks at Hanford and the Savannah River sites. The proposed work is meant to develop a clearer understanding of the advantages and limitations of producing a zeolite-containing waste form (hydroceramic) from calcined radioactive waste, i.e. the effect of processing variables, reaction kinetics, crystal and phase chemistry, and microstructure on their performance.

Research Progress and Implications

Work during the first year of the named grant, has focused on the evaluation of potential starting materials of all kinds in terms of their potential as ingredients for a working waste form formulation. Twenty five parts fly ash (Class C, F, FGD), slag, natural pozzolans (opal, diatomaceous earth,), clays/heat treated clays (kaolinite, montmorillonite, smectite, vermiculite), and zeolites were each mixed with 18 parts of 13 M Na-containing waste simulant (11.5 M NaOH + 1.5 M $NaNO_3$ and 0.069 M CsCl) solutions and cured as above. PCT leaching tests (1 part powder + 10 parts H_2O aged at 90°C for 5-7 hours) narrowed the choice to a limited number of materials. See Table 1 for an

Table 1. Screening Tests of Fly Ashes

Fly Ash	electrical conductivity	%Cs leached
NSP (F FGD)	167	
Midwest Power (C)	134	
Tucson Electric (C)	129	
Hatfield (F)	81	0.35
Holtwood (F)	81	0.35
Montour (F)	52	
PP&L (F)	48	

example of fly ash screening tests. Conductivity was used to test for the amount of sodium leached. It is an efficient way of screening large numbers of samples.

Three types of ash were tested: Class C, F and F containing flue gas desulfurization products (FGD). The best of the lot were the Class F fly ashes. Electrical conductivities are low as are Cs concentrations in the leachates. Typical results of a second type of screening test are given in Table 2. In this instance Rhone Poulenc flash calcined alumina (RP) and condensed silica fume (SF) were added to some of the best starting materials that were determined using Table 1 testing.

The blends used are indicated in Table 2 as follows: for example 21 parts Montour Class F fly ash were blended with 4 parts RP alumina which in turn were blended with 18 parts of the 13M simulant described above. The samples were then cured and tested using PCT protocol as above but in this case samples were soaked for a total of 35 hours. It can be seen that the RP alumina aids in improving the properties of the waste form.

All of the samples listed show promise as potential host formulations for continued testing. The leachates have compositions well within the desirable range for waste forms in general; sodium levels are well below DOE glasses. Efforts are underway to produce more realistic simulated calcines. Two simulants representative of solutions in storage at the Hanford and Savannah River sites are being prepared. Because nitrate is detrimental to the process, it is proposed to calcine some of the LAW at various temperatures (w/wo sugar) to maximize the reactivity of the resultant mix of oxide phases while minimizing the loss of volatiles.

Table 2. Screening of Waste Form Formulations

Pozzolan + RP Alumina ± Silica (SF)	% Na leached	%NO_3 leached	% Cs leached
21 Montour + 4RP	3.6	2.2	0.11
18 Montour + 4RP + 3SF	3.8	5.7	0.1
21 Troy Clay + 4RP	3.6	4.9	0.1
25 Metakaolinite	3.9	18.	0.07
15 Silica Flour + 10RP	2.8	1.4	0.28

Planned Activities

Various calcines containing oxides and traces of nitrate will be mixed with varying amounts and types of the Table 2 formulations, small amounts of other chemicals (alkali hydroxides and/or carbonates, zeolite seeds, templating agents) and enough water to make a paste. The paste can then be cured (in-can) at a variety of temperatures (80°-100°C). Once reaction rates for the process are established, MAS NMR and TEM will be used to study the atomic-level structure of the solids. X-

ray diffraction will be used to examine the degree of crystallinity of the waste forms. On occasion an electron microprobe will be used to analyze the phases in the waste form. Attempts will be made to relate changes in phase chemistry and microstructure to distribution coefficients and dissolution data.

Compressive and bending strength tests will be used to determine mechanical behavior and standard leach tests will be used to determine the potential consequences of cation exchange reactions. Knowing that simulated waste is not an adequate predictor, a major portion of the proposed work will be carried out by Dr. Carol Jantzen at the Savannah River Technology Center; she will run parallel studies using actual LAW samples obtained from the Savannah River site. The value of running parallel studies of this type is self-evident. Given these data, it is expected that it will be possible to piece together a coherent picture of how the crystal and phase evolution of an actual di-phasic zeolite-containing waste form made from LAW governs its performance and its durability once placed into service.

Information Access

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Investigation of Microscopic Radiation Damage in Waste Forms Using ODNMR and AEM Techniques

Project ID: 55367

Dr. Guokui Liu, Argonne National Laboratory

Research Objective

This project seeks to understand the microscopic effects of radiation damage in nuclear waste forms. Our approach to this challenge encompasses studies of crystals and glass containing short-lived alpha- and beta-emitting actinides with electron microscopy, laser spectroscopy, and computational modeling and simulation. Much of our effort is to probe alpha-decay induced microscopic damage in 17-year old samples of crystalline yttrium and lutetium orthophosphates that initially contained ~1% of the alpha-emitting isotope Cm-244 (18.1 y half life). Studies also are conducted on borosilicate glasses that contain Cm-244, Am-241, or Bk-249, respectively. Our goal is to gain clear insight into accumulated radiation damage and the influence of aging on such damage, which are critical factors in the long-term performance of high-level nuclear waste forms.

Research Progress and Implications

This report summarizes work after 2 years of a 3-year project. Using analytic electron microscopic and selective laser spectroscopic techniques, we first examined lanthanide orthophosphate crystals of YPO_4 and $LuPO_4$ that accumulated self-radiation damage from dopant (1 wt.%) ^{244}Cm ions for 17 years. Although the accumulated dose of radiation (>10^{18} alpha-decay events/mg) is significantly high, the samples that we examined physically remain crystalline on a macroscopic scale. Amorphization is not evident, even though isolated defects of various sizes were observed. Microscopic radiation effects in the crystals were manifested by (1) individual defect clusters of 2 to 5 nm size, which resemble disordered fission tracks, and (2) bubbles of 5 to 20 nm that are attributed to accumulation of He atoms generated during alpha decay events. These bubbles are relatively mobile and easily coalesce in electron microsocpy studies due to enhanced diffusion arising from electron irradiation. We have observed that, when exposed to an electron beam, the bubbles aggregated as a function of exposure time. This observation thus provides additional evidence that the bubbles developed from the aggregation of helium atoms that were created from alpha -decay of Cm-244, and the local lattice recovered from radiation damage. In addition to bubbles and fission tracks of nanometer sizes, there exist smaller scale structural defects and lattice strains that were revealed from selective laser excitation and fluorescence spectra. These defects are attributed to alpha-decay induced structural damage that occurred randomly throughout the lattice. Annealing of the samples at 773 K for 12 hours removed most of the residual defects.

Work by others has shown that lanthanide orthophosphates readily undergo amorphization by ion implantation. The lack of amorphization that we have observed in our studies of self-radiation damaged crystals suggests that, (1) recovery occurs simultaneously as damage is produced, and (2) the critical temperature of complete amorphization in the orthophosphate crystals is below room temperature for self-radiation damage induced by alpha decay. The critical temperature determined by ion implantation experiments for these materials is above room temperature. The difference in critical temperatures can be ascribed to the ionization annealing effects associated with the energetic alpha particles generated during alpha decay events. Also, because of the existence of slow annealing (tunneling) processes, the accumulated effects of self-radiation damage induced by radionuclides in waste forms over a long period of time may be different from those observed shortly after ion implantation.

Because of resistance to amorphization under self-radiation, lanthanide orthophosphates are very attractive materials for hosting high levels of long-lived radionuclides, such as Pu isotopes. However, aggregation and mobilization of bubbles might increase the leach rate of such radionuclides and influence the long-term stability of the waste forms. Theoretical modeling and molecular dynamics simulation of radiation-induced damage is being conducted in this project. Accomplishments in theoretical modeling include crystal field calculation for trivalent curium ions in disordered lutetium phosphate and yttrium phosphate lattices, and Monte-Carlo simulation of alpha-decay induced atomic position displacements (amorphization). Our results are consistent with the observations that much of the alpha-decay induced lattice damage has been reversed by self-annealing mechanisms.

Samples of borosilicate glass that contain natural uranium or short-lived actinide isotopes of Am-241, Cm-244, and Bk-249 were prepared as model waste forms and studied in this project with selective laser excitation and X-ray spectroscopy. Our studies have shown that, in borosilicate glasses, actinide ions have ordered structure as to their nearest neighbors. This property allows us to monitor radiation-induced structural damage. After preparation of the glasses samples, selective laser excitation was conducted to probe local environments of the actinide ions, and the same measurements were repeated 4-5 moths later. Extended X-ray absorption fine structure (EXAFS) spectra of the actinide ions in the glass samples also were recorded and analyzed in this project. Based on spectroscopic results, we have established a framework for analyzing radiation damage in this model waste form.

Planned Activities

During the remainder of this project, our effort in molecular dynamics calculation and simulation will be completed. We expect that this effort will provide a theoretical interpretation to the experimental results obtained in this project from studies on the lanthanide orthophosphates and, thereby, materially advance understanding of radiation damage effects in general. Variation in spectral properties, such as inhomogeneous line broadening in the borosilicate glass samples, will be probed periodically. These experimental data will be modeled in computational analyses that will provide a predictive understanding of the long-term effects of radiation damage in high level nuclear waste forms.

Information Access

G. K. Liu, J. S. Luo, S. T. Li, C.-K. Loong, M. M. Abraham, J. V. Beitz, J. K. Bates, and L. A. Boatner, *Scientific Basis for Nuclear Waste Management XXI*, MRS Sym. Pro. **V506**, 921 (1998).

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Stability of High-Level Radioactive Waste Forms

Project ID: 60020

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Lee. D. Trowbridge, Oak Ridge National Laboratory
Karl E. Spear, Pennsylvania State University

Research Objective

The current project is important because of the DOE efforts to increase waste loading of glass waste forms, including the improved understanding of waste components with limited solubility in glass (i.e., phase separation and crystallization) and better models for liquidus temperature due to the current high level of uncertainty. A second area is related to constraints on durability models which can cause acceptable glasses to be rejected. Also considered are issues of species volatility during melter operations and corrosion of melter components and related equipment.

The objective is to develop solution models of complex waste glass systems and spent fuel that are predictive with regard to composition, phase separation, and volatility.

Research Progress and Implications

This report summarizes work after $2^1/_2$ years of the three-year project. An associate model developed in the 1980s was used to represent the thermochemical behavior of liquid/glass oxide solutions. Energies of interaction between end-member component oxides beyond those of ideal mixing often exist and their use in complex systems results in a significant multiplication of terms. These energies are included in the associate model by adding "associate species," with their respective formation energies, to the solution. Thus, the complex interaction terms are embodied in additional species in the solution resulting in a substantially simpler and more easily applied model.

The current work has resulted in the development of a thermodynamic data-file for the quaternary Na_2O-Al_2O_3-B_2O_3-SiO_2 system. The thermodynamic and phase diagram data for six binary (Na_2O-Al_2O_3, Na_2O-B_2O_3, Na_2O-SiO_2, Al_2O_3-B_2O_3, Al_2O_3-SiO_2, and B_2O_3-SiO_2) and four ternary (Na_2O-Al_2O_3-B_2O_3, Na_2O-Al_2O_3-SiO_2, Na_2O-B_2O_3-SiO_2, and Al_2O_3-B_2O_3-SiO_2) subsystems were assessed and optimized. Several liquid associate species were used in modeling the quaternary Na_2O – Al_2O_3 – B_2O_3 – SiO_2 system.

At PNNL there has been concern regarding the precipitation of the nepheline ($NaAlSiO_4$) phase during cooling of certain waste glass compositions. Utilizing the thermochemical computational software and the thermochemical data for the Na_2O-Al_2O_3-B_2O_3-SiO_2 system, the composition space of the ternary oxide Na_2O-Al_2O_3-SiO_2 system was explored at 800°C with no boria present and with 30 wt% boria. The results can be seen in the ternary diagram of Fig. 1 with the binary oxides and the nepheline compositions indicated.

Apparent from the calculational results is the wide compositional range over which nepheline is stable. The maximum silica composition lies along the SiO_2-$Na_2O{\bullet}Al_2O_3$ join. Important for the selection of waste compositions is the observation that the stability region decreases to lower silica content with increasing boria. Experimental results from PNNL at various boria contents are also shown on the diagram, and agree reasonably with the results of the calculations.

Planned Activities

The remainder of the project will be devoted to incorporating the oxides of Fe, Ca, Li, K, Mg, and Ni into the model and its application to the problem of spinel formation in glass melters.

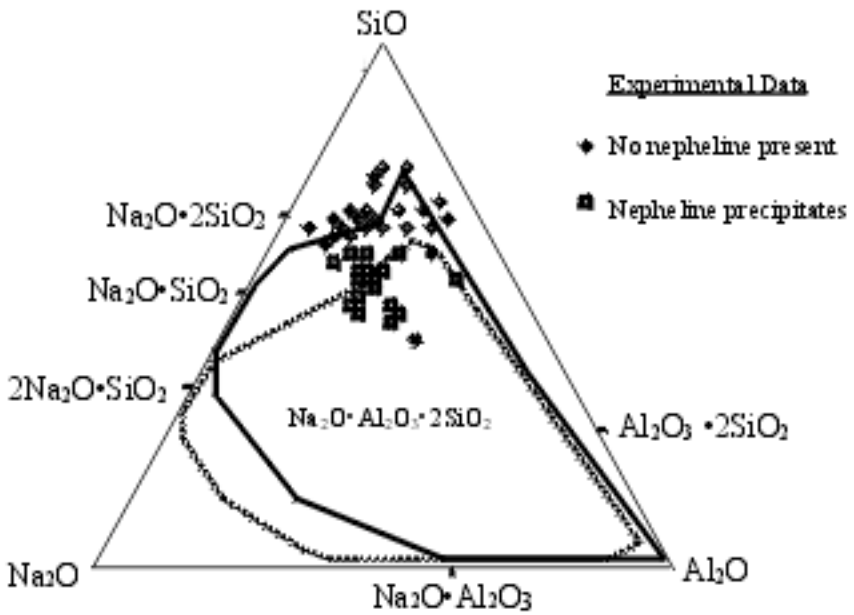

Fig. 1. Ternary Na_2O-Al_2O_3-SiO_2 phase space (wt. %) showing the computed stability region for nepheline plus the glass phase at 800°C with no boria (▬) and 30 wt.% boria (▪▪▪▪) along with experimentally determined precipitation data.

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Mechanisms and Kinetics of Organic Aging in High-Level Nuclear Wastes

Project ID: 65408

Donald Camaioni, Pacific Northwest National Laboratory

Tom Autrey, Pacific Northwest National Laboratory
John Linehan, Pacific Northwest National Laboratory
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Research Objective

Specific DOE problems addressed by this project concern issues arising from organic chemicals in highly radioactive wastes stored at Hanford and Savannah River DOE sites. The organic chemicals, including complexants, are relatively energy-rich such 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 cause changes in 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 to address DOE and regulatory agency requirements for water.

The objective is to develop basic understanding of organic degradation reactions that occur in HLW and assemble models that describe rates and products of degradations. Emphasis is placed on the reactions of complexants and their associated degradation product.

Research Progress and Implications

This report summarizes work after 1.5 years of a 3-year project. The work divides into (1) studies of 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.

1. 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 due to the high concentrations of sodium nitrate and nitrite in HLW, radiation from radionuclide decay ultimately generates NO_x radicals. Since 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.
2. 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 (Ashby et al. *ACS Symp. Ser.* **1994.** *554*, 247-283) 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 mechamism. 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, then 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 is that suggested by Stock (PNNL-11702 Rev. 1, 1997) in which aluminum ion binds both ROH and nitrite ion, thereby fostering intramolecular hydrogen transfer and electron transfer reactions.

3. Solution properties of organic intermediates are being characterized by theoretical methods in collaboration with computational chemists at PNNL's Environmental Molecular Science Laboratory and at 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 the above 3 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.

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

Project ID 65411

Dr. Jun Liu, Pacific Northwest National Laboratory

Dr. David Hobbs, Savannah River Technology Center

Research Objective

The goal of the proposed work is to understand the kinetics of dissolution, precipitation, and scale formation involving Al-containing phases in alkaline salt solutions representative of tank wastes. This research will identify Al-containing phases that are likely to form or be present, and 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 Al-containing phases to form precipitates or scales. Test conditions will 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 gibbiste and boehmite. From the viewpoint of tank waste processing, the dissolution kinetics of gibbsite and boehmite is 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 to boehmite.

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

1. Boehmite is always the stable phase. Gibbsite tends to transform to boehmite.
2. Two fundamental mechanisms were identified for hydrothermal transformation of gibbsite to boehmite:

   (1) 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.

   (2) Dehydration of gibbsite and in-situ nucleation of boehmite on gibbsite. If the reaction was carried out in a 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.

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

   (4) The transformation to boehmite was rapid. Normally an initial incubate time was observed, during which period no boehmite was formed. When the boehmite began to nucleate, the transformation usually was completed within 1 hour.

(5) The existence of high concentration of single salt, of multisalts, such as $NaNO_3$, $Fe(NO_3)_3$, etc., gave rise to a longer incubate time, but did not change the general behavior for the transformation to boehmite.

These results suggest that most aluminum containing phases in tank wastes will be boehmite, and clearly underline the importance of boehmite particles in the dissolution behavior of the tank waste, as well as the colloidal properties of the sludge. Most likely the direct transformation of gibbiste to boehmite in the unsealed container mimics the tank waste condition. However the tank wastes have aged for many years, giving more crystalline particles, with similar particle sizes. In order to predict the efficiency of the tank waste processing (washing and leaching), and to predict 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 speciations. The results obtained will be directly used in a semi-empirical approach to calculate the critical flow velocity needed to transfer the tank waste across the pipelines.

Publication

Jun Liu, Gregg J. Lumetta , Jud W. Virden, Gordon L. Graff, Nancy G. Colton Characterization of Colloidal Phases in Tank Wastes, Proceeding of American Ceramic Society, 1999.

Enhanced Sludge Processing of HLW: Hydrothermal Oxidation of Chromium, Technetium, and Complexants by Nitrate

Project ID: 54765

Steven J. Buelow, Los Alamos National Laboratory

Executive Summary

The Office of Economic Management has identified treatment of High Level Waste (HLW) as the second most costly environmental problem facing the DOE. In order to minimize costs of disposal, the volume of High Level Waste (HLW) requiring vitrification and long term storage must be reduced. Methods for efficient separation of chromium from waste sludges, such as the Hanford Tank Wastes (HTW), are key to achieving this goal since the allowed levels of chromium in the high level glass control waste loading. At concentrations above 0.5 to 1.0 wt.% chromium prevents proper vitrification of the waste. Chromium in sludges most likely exists as the extremely insoluble oxides and minerals, with chromium in the +3 oxidation state. In order to solubilize and separate it from other sludge components, Cr(III) must be oxidized to the more soluble Cr(VI) state. Efficient separation of chromium from HLW could produce significant savings.

This project sought to lay the foundation for the application of hydrothermal processing for enhanced chromium separation from HLW sludges. Experiments were conducted which examined four areas:

a. Oxidation of insoluble Cr(III) solids to soluble Cr(VI) using oxygen,
b. Oxidation of insoluble Cr(III) solids to soluble Cr(VI) using nitrates,
c. Transport properties and speciation of reducing and oxidizing agents under hydrothermal conditions,
d. Reactions of plutonium and americium under oxidizing hydrothermal conditions.

From the results of our experiments in these areas, we have developed a fundamental understanding of chromium speciation, oxidation/reduction and dissolution kinetics, reaction mechanisms, and transport properties under hydrothermal conditions in both simple and complex salt solutions.

Experimental results show that at moderate temperatures (125-200°C), insoluble Cr(III) hydroxide can rapidly be oxidized to soluble Cr(VI). The rate of reaction increases with increasing oxygen and hydroxide concentration and increasing temperature. Experiments also show that sludge components such as aluminate can slow the oxidation/dissolution rate, and that at higher temperatures, organic components in the waste can consume the oxygen before it reacts with the chromium. Reactions of chromium with nitrate only become important at temperatures above 350°C. At lower temperatures the rates of dissolution are not controlled by transport properties. At higher temperatures, particularly near phase transition points, reagent transport could begin to slow and effect dissolution rates. A global rate expression was developed for the reactions involving oxygen and nitrates. The expression agrees well with the experimental results.

Future experiments should examine the reactions of HLW sludges with oxygen at temperatures between 100°C and 200°C at hydroxide concentrations between 1M and 6M. This work should be performed at the Hanford site. Work at Los Alamos will continue, supported by the Nuclear Weapons Program. It will focus on high temperature hydrothermal processes including the oxidation of organic material and TRU salts for purposes of waste minimization and TRU separation.

This project supported nine graduate and undergraduate students from four different universities, one post doctoral fellow, and one visiting faculty member. Collaborations with four faculty members from three university where developed. Seven presentations of this work have already been given at

national scientific meetings, one paper has been published, and three other manuscripts are being prepared.

Relevance, Impact and Technology Transfer

New scientific knowledge focused on critical DOE environmental management problems: The treatment of high level wastes stored in underground tanks is one of the most important challenges facing the DOE. Improvements in the separation of non-radioactive elements, in particular chromium, can greatly reduce the cost of treatment and final disposal. The new scientific knowledge from this project is directly focused on the separation of chromium from inorganic sludges. It provides kinetic data needed to design chromium separation units based on hydrothermal reactions of chromium with oxygen and nitrates. It also provides preliminary information on the effects of other waste constituents, such as organics, hydroxide, and aluminates. The results from this project can also be applied to other DOE management problems. The use of hydrothermal oxidation of TRU metals is being tested at Los Alamos National Laboratory. Collaborative experiments at Los Alamos have already demonstrated that hydrothermal oxidation of TRU contaminated combustible materials produces insoluble TRU metal oxides that can easily be filtered from product effluents. Separation factors of TRU from the combustible material can be as high as 10^7. Most of the combustible material is contaminated with nitrates and many have chromium. The scientific knowledge gained from this project adds to the information needed to elucidate the behavior of metals under oxidizing hydrothermal conditions for the treatment of combustible wastes.

Studies Related to Chemical Mechanisms of Gas Formation in Hanford High-Level Nuclear Wastes

Project ID: 54807

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Charles L. Liotta, Georgia Institute of Technology
Henry M. Neumann, Georgia Institue of Technology

Research Objective

The objective of this work is to develop a detailed mechanistic understanding of the thermal reactions that lead to gas production in certain high-level waste storage tanks at the Hanford, Washington site. Prediction of the combustion hazard for these wastes and engineering parameters for waste processing depend upon both a knowledge of the composition of stored wastes and the changes that they undergo as a result of thermal and radiolytic decomposition. Since 1980 when Delagard[1] first demonstrated that gas production (H_2 and N_2O initially, later N_2 and NH_3) in the affected tanks was related to oxidative degradation of metal complexants present in the waste, periodic attempts have been made to develop detailed mechanisms by which the gases were formed. These studies have resulted in the postulation of a series of reactions[2] that account for many of the observed products, but which involve several reactions for which there is limited, or no, precedent. For example, $Al(OH)_4^-$ has been postulated to function as a Lewis acid to catalyze the reaction of nitrite ion with the metal complexants, NO^- is proposed as an intermediate, and the ratios of gaseous products may be a result of the partitioning of NO^- between two or more reactions. These reactions and intermediates have been the focus of this project since its inception in 1996.

Research Progress and Implications

During the first 32 months of this 48 month project (a 12 month extension has been requested) the primary focus has been toward (*1*) the development of precursors that would allow NO^- to be generated rapidly and under controlled conditions, (*2*) further development of models for aluminum catalyzed nitrite oxidation of HEDTA, and (*3*) an analysis of the relative contributions of thermal vs radiolytic pathways for complexant decomposition in tank 101-SY.

(*1*) *Precursors* to NO^- (A. Belcher, graduate student). The NO^- anion, like isoelectronic O_2, can exist in either the singlet state or the triplet state. Contrary to the considerable experimental and theoretical work on NO^- and its conjugate acids in the gas phase, relatively little is known about the anion in condensed phases although one theoretical study indicates that the triplet state is also the ground state of $(NO\bullet 2H_2O)_{(g)}^{-3}$. Our objective is to discover methods to rapidly generate NO^- in condensed phase under controlled conditions. Earlier attempts to thermally and photochemically decompose **A** indicated that neither reaction was sufficiently rapid for our purposes. Reaction of hydrochloride salt of **A** with 2 equiv of BuLi in THF yielded $Li_2N_2O_2$ but the reaction is relatively slow (hr). More promising are reactions of **A**•HCl in DMSO with dimsyl anion ($CH_3SOCH_2^-$), produced using BuLi or NaH, which appear to occur quite rapidly although the results have not been entirely reproducible. These reactions have been monitored using a colleague's spectrofluorometer, which is available only occasionally. An instrument has been ordered that can be devoted exclusively to this project.

We plan to examine the base induced decomposition of **A**•HCl in the presence of potential trapping agents (PhCHO, $Ni(CN)_4^{2-}$, dienes) for NO^- during the next few months. A manuscript describing a low-cost, convenient synthesis of 9,10-dimethylanthracene, a precursor to **A**, is in preparation.

Methods to obtain NO^- by rapid electron transfer from strong reducing agents are under investigation. Possible reductants studied to date have included photochemically excited $Ru(bipy)_3^{2+}$ in aqueous solution and sodium naphthalide in THF. Quenching of fluorescence of $Ru(bipy)_3^{2+}$ was initially observed, but this was ultimately traced to impurities in the NO. In the course of this excursion, we discovered that the spectrum attributed to NO in aqueous solution[4] is actually due to HONO. The products from the sodium naphthalide reaction are still under investigation, but the reaction is fast and most of the naphthalene can be recovered from the product mixture by sublimation.

A paper describing our study of the kinetics of decomposition of Piloty's acid ($PhSO_2NHOH$), a precursor for NO^- has been submitted for publication.[5] As indicated in last year's report, our interpretation of the kinetics requires the participation of tautomeric forms of the monoanion of the acid. In view of the conclusion based upon Overhauser enhancements in the nitrogen NMR spectrum that the monoanion was O-deprotonated[5] we attempted to acquire chemical evidence for the structure of the anion by alkylation experiments under basic conditions. We did obtain NMR spectral evidence to suggest that the anion could be trapped by alkylation with acrylonitrile, but the structure of the alkylated product could not be assigned directly by its NMR spectrum. Unfortunately attempts to independently synthesize the possible alkylated products failed and this approach was abandoned.

(2) *Development of models for aluminum catalyzed nitrite oxidation of HEDTA* (Greg Lavaty, graduate student). A focus of work in this area during the past year has been on the synthesis and study of aluminum nitrite compounds, which are currently unknown. Lavaty, a new graduate student in our group for six months during the year, did exploratory studies on the reaction of $AlEt_3$ with several reagents:

N_2O_3 in CH_2Cl_2 at -20 °C → no reaction (1)
$N_2O_3 + H_2O$ in CH_2Cl_2 at -20 °C gas evolution but the product was predominantly nitrate (2)
[quinuclidineH]Cl/CH_2Cl_2 + $AlEt_3$ → gas evolution; apparently formation of quinuclidine•$AlCl_3$ (3)
[quinuclidineH]Cl/CH_2Cl_2 + $AgNO_2$ → mixture of $[quinuclidineH]^+$ nitrite and nitrate (4)

N_2O_3 was generated by passing gaseous NO through the CH_2Cl_2 solution of N_2O_4/NO_2 at -20 °C to give the characteristic blue color. The results of reaction (2) suggest that conversion to HONO was not complete, if in fact, it actually occurs. A review of the literature is somewhat ambiguous on this conversion in condensed phases. Reaction (3) was done in preparation for the examination of the comparable reaction with the nitrite salt, which we anticipated making according to (4). Unfortunately several attempts at reaction (4) with multiple batches of both reagents has given products whose ^{14}N NMR spectra indicate gross contamination by nitrate. Exactly how nitrate is produced is unknown. Unfortunately Lavaty has left the graduate program; Further investigation of this chemistry will be undertaken by an undergraduate student during the summer.

(3) *Analysis of the relative contributions of thermal vs radiolytic pathways for complexant decomposition in tank 101-SY*. A brief summary of the results of this analysis was given in the 1997 progress report. No further work has been done since.

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Colloidal Agglomerates in Tank Sludge: Impact on Waste Processing

Project ID: 54628

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Dr. James Martin, Sandia National Laboratories - Albuquerque
John D. Berg, University of Washington

Research Objectives

Insoluble colloidal sludges in hazardous waste streams such as tank wastes can pose serious problems for waste processing, interfering with retrieval, transport, separation, and solidification processes. Properties of sediment layers and sludge suspensions such as slurry viscosities, sedimentation rates, and final sediment densities can vary by orders of magnitude depending on the particle types present, the degree to which the particles agglomerate, and processing parameters such as shear rates, pH, salt content, and temperature. The objectives of this research are to

- understand the factors controlling the nature and extent of colloidal agglomeration under expected waste processing conditions
- determine how agglomeration phenomena influence physical properties relevant to waste processing including rheology, sedimentation, and filtration
- develop strategies for optimizing processing conditions via control of agglomeration phenomena.

Complex radioactive mixtures of supernatant liquids (typically highly basic salt solutions), saltcake (consisting primarily of sodium nitrate and nitrite), and insoluble sludges consisting of submicron colloidal particles are stored at various locations on U.S. Department of Energy (DOE) sites. Over 100 million gallons of this radioactive waste is stored in underground tanks. The largest quantity and most complex mixtures of these radioactive wastes are located at the Hanford Site. Although the radioactivity is the primary concern in remediating these wastes, handling and processing the radioactive insoluble sludges provides a major technical challenge. Treatment and ultimate disposal of these wastes will require that these insoluble sludges be dispersed in aqueous solutions for retrieval and transport, separated from the liquid, and converted to a stable waste form. These tank wastes will be partitioned into high-level and low-level fractions because of the high cost of high-level waste vitrification and geologic disposal. The low-level fraction will be processed to remove ^{137}Cs (and possibly other radionuclides) and will then be immobilized in a glass matrix and disposed of by shallow burial on site. The high-level fraction will be immobilized in a borosilicate glass matrix, and the resulting glass canisters will be disposed of in a geologic repository. The maximum possible solids loading in each of the processing steps and the final waste forms are desired to minimize waste volumes.

The ability to maximize the solids loading and effectively process the wastes is dependent upon understanding and properly manipulating the colloidal behavior in these waste streams. Depending on processing conditions, these colloidal particles can form agglomerated networks having high viscosities that could clog transfer lines or produce high volumes of low-density sediments that interfere with solid-liquid separations such as settle-decant operations during sludge washing and leaching. Under different conditions, the particles can be dispersed to form very fine suspended particles that do not settle during settle-decant operations. These suspended particles may foul and contaminate downstream components such as ion exchangers or filtration systems. The formation and properties of viscous sludge layers also contribute significantly to the retention and periodic release of potentially flammable or explosive gas mixtures in some Hanford tanks. Colloidal

agglomerates are also important to the processing and remediation of other waste streams, including the sludges present in fuel storage basins such as the K-Basins at Hanford.

Given the wide range of waste chemistries present at Hanford and other DOE sites, it is impractical to measure the properties of all possible sludge compositions under all potential processing conditions to design effective treatment procedures. Instead, a framework needs to be established to predict sludge property trends on a sound scientific basis. The underlying principles of colloid chemistry and physics provide such a framework, allowing us to predict and eventually control the physical properties of sludge suspensions and sediment layers in tank wastes and other waste processing streams.

Research Progress and Implications

This research project combines experimental and theoretical efforts to determine the impact of colloidal agglomeration on tank waste processing. Components of this research program include 1) understanding the nature of the primary particles and agglomerates that comprise tank sludge, 2) determining how particle and agglomerate distributions influence the physical properties of sludge, 3) understanding the critical interparticle interactions that control agglomerate distributions and slurry properties, and 4) developing chemical and physical methods to deliberately manipulate agglomerate structures during different waste processing steps. Work on the first two items was largely completed in FY 1997 and FY 1998. Work is in progress to understand how interparticle interactions influence agglomeration and sludge properties. A summary of the progress on items 1 and 2 is provided in this report, but the majority of the report will address items 3 and 4.

Particles and Agglomerates in Actual Tank Sludge

Work done prior to this year demonstrated that Hanford sludges consist largely of submicron ($<10^{-6}$ m) primary particles of hydrated oxides of Al, Fe, U, Zr, Mn, Cr, Ni, and Ti. Small particles of insoluble salts such as apatite $Ca_5(PO_4)_3OH$, uranium phosphate, aluminum phosphate, bismuth phosphate, and the zeolite cancrinite are also present. In existing tanks, and in most proposed tank processing schemes, the particles are in contact with highly basic (pH 10-14), high ionic strength (0.1-10 M) salt solutions (mainly $NaNO_3$ and NaOH). In such solutions, the electrical double layers associated with charged sites in particle surfaces collapse, and the electrostatic repulsions that can disperse particles of like charge disappear. Therefore, under most tank waste processing conditions, the particles comprising most sludges are predicted to be attracted to each other (van der Waals attraction dominates) resulting in extensive particle agglomeration. Most of the work performed in this project involves examining model suspensions containing mixtures of one or two of the major components found in actual wastes and studying how agglomeration influences physical properties such as viscosity and sedimentation. Experimental results on the simple systems are rationalized using theoretical models that describe particulate suspensions. Property models developed from theory and experiment on the simple suspensions are then applied to explain the limited results that have been obtained on actual tank wastes.

Rheological and physical data have been obtained on samples from 17 single-shell and 10 double-shell tanks. Many of these samples were processed to simulate the baseline processes proposed for ultimate disposal of these tank wastes. Physical properties and rheology have also been measured on these process samples. The results from these analyses have been compared with the results obtained on the simple systems used in this project. Large variability is observed in the properties of the waste in the tanks. This variability is also observed within an individual tank. In spite of this variability, the experimental results obtained for simple surrogate systems are comparable to actual tank waste samples under similar conditions.

The capabilities developed in this project have been used in obtaining more detailed physical properties on actual tank waste sludges and other radioactive waste samples such as K-Basin sludges. Extensive particle size distribution, sedimentation behavior, and particle density data have been obtained on samples from Hanford tanks 241-AW-101, 241-AN-107, and 241-AN-105 using the equipment and knowledge obtained in this project. Significant processing issues of the K-Basin sludges have been resolved based on data obtained and understood because of the research efforts

associated with this project. Particle size distribution of samples obtained from the gunite tanks at ORNL is currently being considered at PNNL using these capabilities.

Agglomerate Structures: Impact on Sludge Properties

The properties of agglomerated sludges are dominated by the properties of the agglomerates, which are fractal objects whose mass scales as R^D, where R is the agglomerate size and D is the fractal dimension. For a diffusion-limited aggregate, D = 1.8; D = 3.0 for a dense three-dimensional object. Fractal agglomerates can have an enormous impact on slurry properties because they have lower densities and occupy much more space than dense particles at the same solids loading. The solids loading within an individual agglomerate, Φa, is given by the expression $\Phi a = (R/r)^{D-3}$, where r is the primary particle size. As shown in Figure 1, Φa can vary over three orders of magnitude depending on the ratio of the agglomerate size to the primary particle size and the fractal dimension. When agglomerates fill the solution and begin to contact each other (at a solids loading referred to as the percolation threshold or gel point ($\Phi g = 0.17\ \Phi a$), slurry viscosities can increase by orders of magnitude. Sediment densities are usually not much greater than Φg because sedimentation rates are slow to negligible above the gel point. Work on this project has shown that fairly accurate values for Φg can be calculated for both single component slurries and actual tank wastes if r, R, and D are determined experimentally.

For this program, primary particle size distributions have been determined using transmission electron microscopy, and agglomerate size distributions have been estimated using static light scattering on dilute suspensions. Direct measurements of the fractal dimension D have not been made, but based on literature studies on model systems, D = 2.2 has been used to model slurry properties (the theoretical value for a rearranged reaction-limited aggregate). Using experimental r and R values and D = 2.2, sediment densities have been predicted to within about 20% for single component systems as well as actual sludges, solids loadings at which slurry viscosities will exceed the desired maximum of around 100 cP have been predicted to within about 30%, and sedimentation velocities in settle-decant operations have been predicted to within a factor of around 5. In terms of general trends, the least tractable slurries are those containing the smallest primary particles (10 nm particles are common in actual tank sludges), the largest agglomerate sizes, and the smallest fractal dimensions.

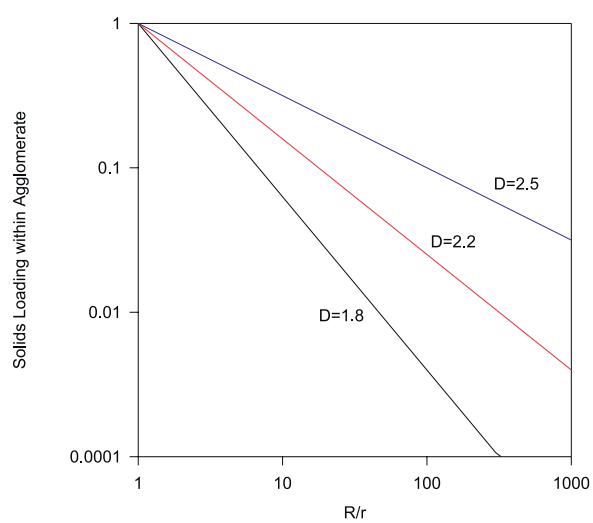

Figure 1. Solids Loading Within Fractal Agglomerates as a Function of R/r and D.

Such slurries can have viscosities in excess of 10,000 cP at solids loadings as low as 1 vol%, which corresponds to the lowest sediment densities. At the other extreme, slurries containing primary particles larger than 10 μm can exhibit viscosities below 100 cP even at 30 vol% and pack to form dense sediments having solids loadings that exceed 35 vol%. Of the 20 or so distinct Hanford wastes examined to date, most exhibit gel points from 1-8 vol%. For the finest sludges, dilution factors as high as 20 may be required to keep from plugging pipes and transfer lines with viscous colloidal gels, generating millions of gallons of additional waste requiring treatment and ultimate disposal.

Interparticle Interactions: Impact on Sediment Densities

The focus of research during FY 1998 and FY 1999 has been on achieving an understanding of the relationships between interaction potentials and sediment densities in the high-salt, high-pH regime representative of most tank wastes. Work done prior to FY 1998 showed that changes in salt content representative of sludge washing and leaching operations can change sediment volumes by as much as a factor of two, having an enormous impact on processing tank utilization and separation efficiencies. Our practical goal is to be able to predict and control sediment densities in basic salt solutions. This regime is also of significant scientific interest because interaction potentials in such solutions cannot be described using classical electrical double-layer theory (the double layers collapse in high ionic strength solutions).

The macroscopic physical properties for a particular colloidal particle gel depend on both the gel microstructure and the interparticle forces. One example of a gel property is the compressive yield stress, $P_y(f)$, which is a measure of the force required to compact a gel network to a specified volume fraction, ϕ. The compressive yield stress controls both the final sediment height of a colloidal suspension and the rate at which the sediment compresses to reach that final height. A model has been developed to calculate the compressive yield stress as a function of gel microstructure and interparticle forces using the Brownian dynamics simulation method.

In this model, the initial particle network configuration was created using Brownian dynamics. A random distribution of noninteracting particles is formed using a series of Monte Carlo moves. Brownian motion then moves the individual particles or particle clusters until contact is made with another particle or cluster. The two are then combined to form a rigid cluster, which then has translational and rotational diffusion based on cluster size. This procedure continues until a continuous gel has been formed. The first series of three-dimensional colloidal gel models consisted of 10,000 particles and was created assuming diffusion limited aggregation. Gels were created for 2.0, 4.0, 6.0 and 8.0 vol%. A sample gel configuration is shown in Figure 2.

Once a gel configuration has been created, the rigid bonds are replaced with an interaction potential, which consists of both a repulsive core potential and a surface-bonding interaction. The core potential is based on the distance between particle centers. The surface-bonding interaction prevents a connecting particle from freely moving around the circumference of its partner, giving the gel its rigidity. The specified potential well depth determines the surface interaction strength. When the surface-point to surface-point distance exceeds a specified value, the connection is broken. If two particles move within the cutoff distance, a new connection is formed.

The compressive yield stress as a function of volume fraction is determined by performing a compression simulation on the gel structure and calculating the resulting stress tensor. The compression simulation is performed using a repeating sequence of two stages, a compression stage and an equilibrium stage. During the compression stage, the scaling factor is gradually reduced in a linear fashion. The rate of reduction depends on a variety of factors, including the potential well depth and temperature. During this stage, interparticle connections are broken and new ones are created as the gel network structure changes to accommodate the reduction in volume. After a period of time, the scaling factor is held constant and the system is allowed to reach equilibrium. The approach to equilibrium is monitored using the calculated values of the stress tensor. Once the system has reached equilibrium, quantities such as the stress tensor and the coordination number are calculated for that volume fraction. This procedure is repeated until the volume fraction reaches a specified value. The calculated stress is then plotted as a function of volume fraction. Preliminary results have been obtained for the initial volume fractions listed for a single form of the interparticle potential.

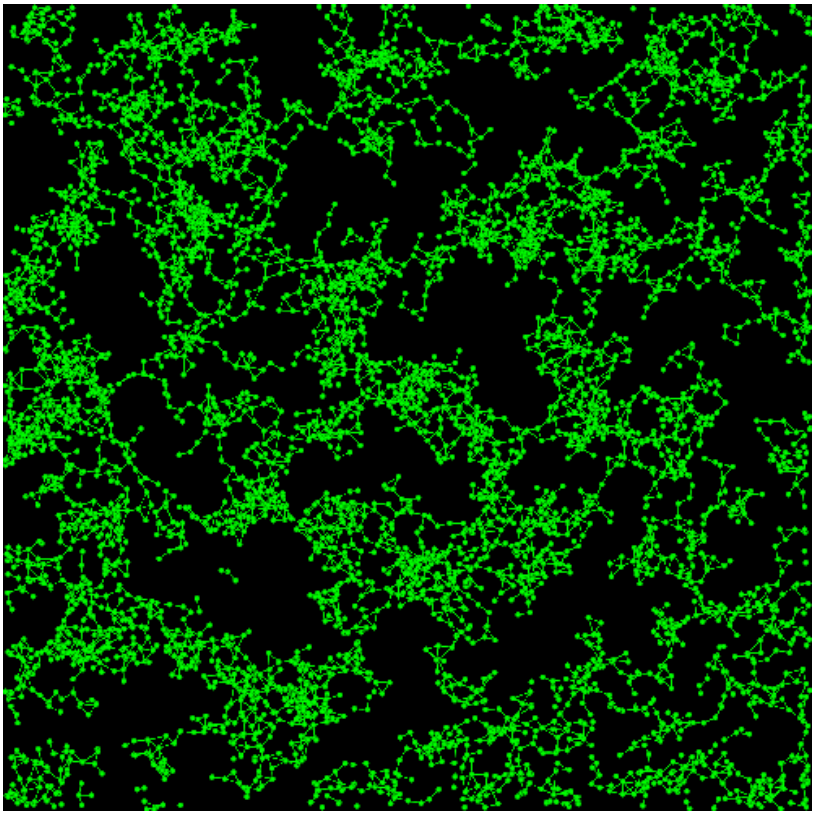

Figure 2. Initial Particle Gel Configuration from Brownian Dynamics Simulation

This simulation methodology provides a direct connection between the microscopic interparticle interaction potential, which is not directly measurable, and the macroscopic gel property compressive yield stress, which can be obtained from sedimentation experiments. By varying the interparticle potential and comparing the change in the compressive yield stress with experimental results, we may be able to infer the effect of changes in solution chemistry on the interparticle potential.

Sedimentation experiments were performed at varying solids loadings, pH, salt concentration, salt type, and applied pressure to determine the impact of chemical processing on the sediment densities that can be obtained during settle-decant processes. These results are also being compared with the models being developed. Based on these results, it is possible to extract values for the gel point and the compressive yield stress of the sediment (which is a measure of how deformable and compressible the sediment is.) Once these parameters are known, sediment densities can be predicted for a wide range of processing geometries, including extrapolation from lab-scale tests to sedimentation in a one-million-gallon tank.

Sedimentation studies were conducted on 1.3 µm primary particles of gibbsite ($Al(OH)_3$) suspended in sodium nitrate solutions at different salt concentrations and pH values. At pH 4 and 0.01 M $NaNO_3$, the primary particles of gibbsite are dispersed. Because the particles are relatively large, they settle within a few days. The dispersed particles pack efficiently as they settle, yielding a sediment with a density of 50 vol% (the theoretical maximum solids loading for packed spheres is 63 vol%). Such a sediment would be ideal for maximizing the efficiency of solid-liquid separations. In contrast, the same gibbsite particles suspended in 0.1 M $NaNO_3$ at pH 4 yield a sediment density of only 4 vol% solids (consistent with 6-7 µm fractal agglomerates each containing around 30 primary particles). This means that the agglomerated sludge occupies over 10 times more space and contains 24 times the volume of non-removable interstitial liquids than the sediment formed from the dispersed sludge, having an adverse impact on the efficiency of solids-liquids separations. As salt concentrations are increased still farther, to 5 M, sediment densities increase to 5.1 vol%, suggesting that "short

range" or "hydration" forces associated with adsorbed salt layers might be weakening the interactions between particles. High salt concentrations could also change sediment densities by changing agglomerate structures.

To investigate the role of adsorbed ions on interparticle interactions, systematic variations were made in the cations and anions present in dissolved salts to examine whether specific ions were more effective than others in weakening sediment structures. Gibbsite particles were suspended in aqueous solutions containing various salts ($NaNO_3$, NaCl, CsCl, LiCl, $Mg(NO_3)_2$, $CaCl_2$, and $BaCl_2$) as a function of pH (pH 4–14) and salt concentration (10^{-2} M–5 M) (Figure 3). All salts tested promote sediment compression at concentrations above 1 M. While anion (Cl^- for NO_3^-) and cation (Li^+ or Cs^+ for Na^+) substitutions have no apparent effect, salts of divalent cations (Mg^{2+}, Ca^{2+}, Ba^{2+}) all promote sediment compression. Most dramatic is the effect of $CaCl_2$, which yields sediments having solids loading of over 15 vol% (twice the particle density seen in $NaNO_3$ solutions). The effect is not merely an ionic strength effect, because $BaCl_2$:NaCl mixtures having the same ionic strength but different Ba:Na show greater compression as the Ba content is increased. The results suggest that heavily hydrated cations can act as "molecular ball bearings," allowing agglomerates to deform and compact. The results represent one example of how it may be possible to use chemical additives to control sludge behavior.

As is shown in Figure 4, pH has a significant impact on the sediment densities obtained during settle-decant operations. The lowest sediment density is observed near the isoelectric point of the particle with the sediment density increasing on either side of the isoelectric point. The isoelectric point of a particle is the pH value at which a reversal of the charge on the particle is observed electrophoretically. Zeta potential is the potential of the particle at the surface of shear and is related to the electrophoretic mobility of the particle; therefore, a measurement of the zeta potential of a slurry as a function of pH will provide insight into the impact of pH on the sediment densities that would be obtained during settle-decant operations.

Zeta potential measurement of colloidal dispersions at high salt concentrations is a new and unexplored scientific area with many reported departures from expected theory, including elimination of the isoelectric point and restabilization of colloidal particles with adsorbed surfactants.

Zeta potential is experimentally determined by measuring the motion of particles in solution under an applied electric field. Traditionally, these measurements are performed at low ionic concentrations due to experimental difficulties at high salt concentrations. The ZetaPals is designed to permit the

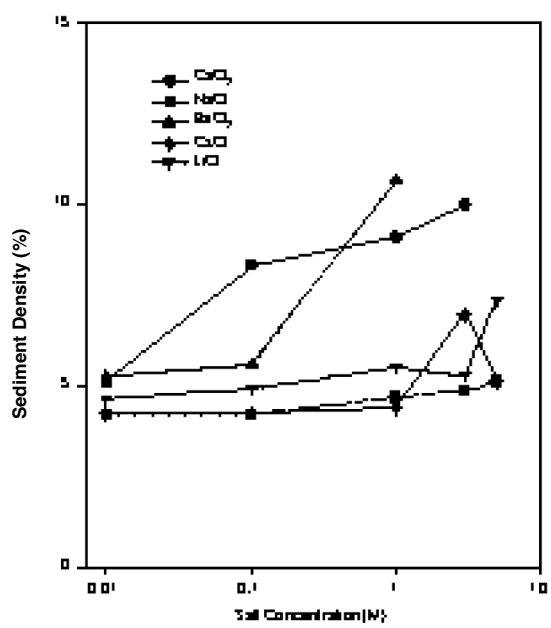

Figure 3. Impact of Salt Concentration and Type on Sediment Density

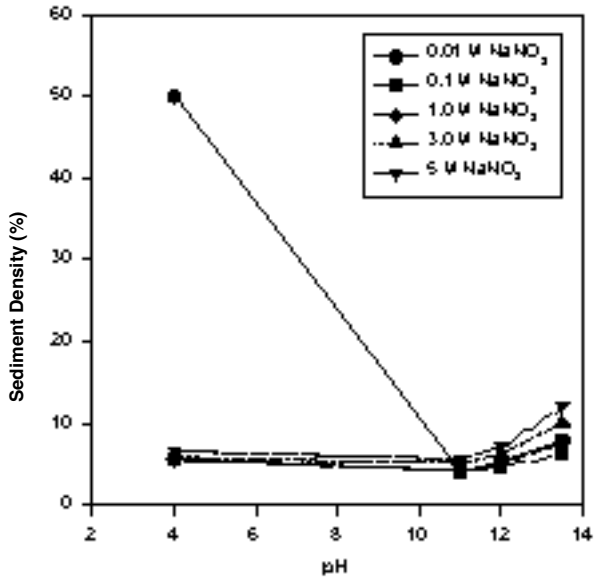

Figure 4. Impact of pH and Salt Content Salt on Sediment Density

measurement of zeta potential at high salt concentrations. These measurements are still problematic and require attention to establishing the proper experimental conditions (voltage, frequency, and sample count rate) and expertise combined with common sense in interpreting the results. The high conductivity of the concentrated salt solutions limit the voltage and current that can be applied to the solution while still imparting movement of the particles due to the applied electric field. If too high a voltage is applied, water is broken down to hydrogen and oxygen at the anode and cathode respectively. If too high a current is applied, the sample is heated and fluid-flow gradients are created that disturb the measurement of particle motion.

Over the last several months, the zeta potential of alumina (0.01 wt %) in water, $NaNO_3$, and LiCl has been measured. Zeta potential measurements of alumina in water as a function of pH compared well with values reported in the literature. Zeta potential measurements of alumina in $NaNO_3$, as a function of pH, at higher salt concentrations were then undertaken. Measurements were made at 0.1, 1.0, 2.0 and 3.0 M $NaNO_3$.

Results suggest that at the lower salt concentration (<2.0 M) double-layer theory is observed. This implies that the double layer has collapsed and that the system rapidly aggregates, forming a loose floc network of particles that exhibit a fast sedimentation time and a large sedimentation volume. Initial zeta potential measurements on alumina at 3.0 M $NaNO_3$ suggest that the particle dispersion is restabilized and that the isolelectic point (point of zero charge) is not present. The particles exhibit a positive zeta potential over the entire pH range investigated. This implies that the particles do not aggregate into a loose floc network and will exhibit a smaller sedimentation volume. This has been confirmed by previous sedimentation results.

The implication of this work is that the colloidal properties of tank waste under high salt conditions (greater than 2.0 M) may not behave as expected. If colloidal tank waste is in fact restabilized under high salt conditions, particle size may be smaller than expected, sedimentation time and volume may be different than expected, and filtration properties may be different.

Work performed on this project at the University of Washington is being directed at understanding how organic molecules called steric stabilizers function in the high salt regime of tank wastes. Once the factors controlling steric stabilization at high ionic strength are understood, it may be possible to manipulate sludge behavior with low concentrations of such organic additives. The polymers used as steric stabilizers were BAB block copolymers of polyethylene oxide B blocks and polypropylene oxide A blocks. The B blocks are the stabilizing moiety, and the A blocks anchor the polymer to the laytex surface. The core particle is a polystyrene latex with sulfate functional groups that allow the polymers to anchor to the core particle.

The impacts of polymer molecular weight, salt concentration, and salt type on steric stabilization were investigated. Increasing the molecular weight of the polymer causes an increase in steric stabilization. A small increase in molecular weight from an 11-monomer-length polymer to a 13-monomer-length polymer, showed dramatic increases in stabilization of the particle. This increase may be due to ion binding of the salt in the longer polymer that is not possible in the shorter polymer. Results obtained from the 13-monomer-length polymer indicate that order of stabilization in high ionic strength solutions is $BaCl_2$ > $NaNO_3$, LiCl, NaCl, KCl > KSCN, KNO_3. X-ray photoelectron spectroscopy (XPS) and RAMAN spectroscopy were performed on this same system in both KSCN and $BaCl_2$ to understand the processes that cause stabilization to occur in $BaCl_2$ and not in KSCN solutions. The results from these studies indicated that the Madelung shift (a constant representing the sum of the mutual potential coulombic attraction energy of all the ions in a lattice) correlates with the order in which the anions induce restabilization of these particles. It was also observed that $BaCl_2$ tends to weaken the ether oxygen bonds in the polyethylene oxide more than the KSCN, but the conformation of the polyethylene oxide is the same in both the KSCN and $BaCl_2$ solutions.

Planned Activities

Several key studies are in progress and will be completed before the end of FY 1999. These studies include a comparison of the actual waste rheology and sedimentation with the simple model systems, measurement of short-range forces, and modeling of agglomerate properties.

A report compiling the rheology data that has been collected on actual wastes and comparing these results with the data obtained by simple model systems will be prepared. This report will provide the basis for further improvements in rheological measurement of actual tank wastes.

Now that a simulation methodology has been established for predicting compressive yield stress based on gel structure and interparticle potentials, a parametric study will be performed to determine the effect of changes in the interparticle potential on the compressive yield stress behavior of a sediment. This information will be used to infer the effect of solution chemistry on the interparticle potential by comparing simulation results with experimentally determined compressive yield stress values.

Samples of the polystyrene latex particles with steric stabilizers attached have been submitted to NIST for surface force measurements. These measurements will be used to determine the magnitude of the short-range hydration forces in high ionic strength solutions. Samples have also been submitted for nuclear magnetic resonance analysis to better understand ion binding in these model systems. Equilibrium dialysis, solvent extraction or specific ion electrode analysis will also be performed to quantitate the extent of ion binding.

Information Access

Publication

Bunker BC, J Liu, DR Rector, GL Graff, PA Smith, PJ Bruinsma, L Song, XS Li, JD Virden, NG Colton, JR Philips, KD Keefer, and JM Tingey. 1999. "Fractal colloidal agglomerates in nuclear tank wastes: Impact on waste properties and processing" (submitted to *Radioactive Waste Management in Environmental Restoration*).

Presentations

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Tingey JM, BC Bunker, GL Graff, KD Keefer, AS Lea, and DR Rector. November 1998. "Colloidal agglomerates in tank sludge and their impact on waste processing." Materials Research Society Fall Meeting, Boston.

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Investigation of Novel Electrode Materials for Electrochemically-Based Remediation of High- and Low-Level Mixed Wastes in the DOE Complex

Project ID: 55137

Dr. Nathan S. Lewis, Caltech

Research Objectives

One of the key issues that must be solved to achieve a successful remediation of the high level liquid wastes (HLW) at the Hanford and at Savannah River sites is the removal of the significant quantities of nitrate and nitrite in the existing liquid waste streams that are presently on these sites in the DOE complex. One method of waste stream remediation is electrochemical oxidation, which is an in-situ method that has been well-documented to have significant advantages in many areas with respect to pump-and-treat approaches to waste remediation. There are, however, significant aspects of the electrochemical oxidation process that need to be addressed from a basic research viewpoint. The research being performed under this proposal will investigates new materials, initially based on degenerately-doped titanias, for use in the electrochemical degradation of organics and nitrogen-containing compounds in sites of concern to the DOE remediation effort.

Research Program to Investigate the Fundamental Chemistry of Technetium

Project ID: 60296

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Research Objective

Technetium (^{99}Tc, half-life = 2.13x10^5 years, β-emitter) is one of the radionuclides of major concern for nuclear waste disposal. This concern is due to the long half-life of ^{99}Tc, the ease with which pertechnetate, TcO_4^-, migrates in the geosphere, and the corresponding regulatory considerations. The problem of mobility of pertechnetate in the environment is compounded by the fact that pertechnetate is the thermodynamically stable form of technetium in oxidizing environments. Because of this stability, pertechnetate was presumed to be the predominant chemical form of technetium in the aqueous phase of nuclear waste tanks. However, recent studies indicate that a significant fraction of the technetium is in a different chemical form.[1,2] These factors present challenges for the disposition of technetium.

Research Progress and Implications

Radiation chemistry of technetium in alkaline solution. As of February, 2000, our efforts have principally focused on exploring the radiation chemistry of pertechnetate in alkaline solution with added organic compounds, nitrate, and/or nitrate. The most important results are 1) the chemistry and identity of the organic radicals control the rate of reduction of pertechnetate during radiolysis, and 2) organic radicals can reduce pertechnetate even if a large excess of nitrate or nitrite is present.

Radiolysis in water at high pH produces mainly e^- and O^- as the primary radiolysis products. At high pH, the radiation-chemical yields, G, of e^- and O^- are $G_e \cong G_o = 0.32$ mmol J^{-1}. The hydrated electron, e^-, reacts quickly with TcO_4^- to give TcO_4^{2-}; e^- also reacts quickly with NO_3^- and NO_2^-. Because nitrate and nitrite react quickly with e^-, reduction of TcO_4^- by e^- is strongly suppressed in solutions with high [NO_3^-] or [NO_2^-]. The oxide radical ion, O^-, reacts rapidly with organic molecules by H-abstraction to give organic radicals. Organic radicals can reduce TcO_4^- in the presence of a large excess of nitrate or nitrite since organic radicals react very slowly with NO_3^- and NO_2^- but react quickly with TcO_4^-.[3,4] Consequently, radiolysis can reduce TcO_4^- even in high concentrations of nitrate and nitrite. Figure 1 shows $G(-TcO_4^-)$ for radiolysis of solutions of 200μM TcO_4^-, 2M NaOH, 0.1M iminodiacetate (IDA), and varying concentrations of nitrate or nitrite. In addition, Figure 1 shows calculated $G(-TcO_4^-)$, which were determined using a rate law derived from the reaction scheme illustrated in Figure 2. The most important result shown in Figure 1 is the fact that $G(-TcO_4^-)$ approaches a limiting value as [NO_3^-] increases. This limiting value, 0.006 μmol J^{-1}, is presumably the radiation-chemical yield for reduction of the TcO_4^- by the carboxy(carboxymethylamino)methyl radical generated by H-abstraction from IDA.

Identity of Radiolysis Products.[5] Radiolysis of alkaline solutions of TcO_4^- in the presence of ethanol, ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA), IDA, or citrate produces an insoluble precipitate. This material has a characteristic electron paramagnetic resonance (EPR) spectrum, which is shown in Figure 3. Figure 3 also shows the EPR spectrum of $TcO_2 \bullet xH_2O$ produced

by hydrolysis of $TcCl_6^{2-}$. The EXAFS spectra and Fourier transforms of the insoluble radiolysis product and $TcO_2 \bullet xH_2O$ are shown in Figure 4. Because the EPR and EXAFS spectra of the insoluble radiolysis product and $TcO_2 \bullet xH_2O$ are the same, we conclude that the insoluble radiolysis product is simply $TcO_2 \bullet xH_2O$. This result shows that the Tc(IV) complexes of EDTA, NTA, IDA, or citrate are not stable in highly alkaline solutions.

Radiolysis of TcO_4^- in 2M NaOH in the presence of glyoxylate ($^-O_2CCHO$), formaldehyde, or ethylene glycol produces pink solutions with no precipitate. These solutions all have weak absorption peaks at 500 nm in their UV/Vis spectra, similar to $(EDTA)_2Tc_2(\mu\text{-}O)_2$.[6] The EXAFS spectrum of one of these solutions is shown in Figure 3d. The EXAFS spectrum of $(EDTA)_2Tc_2(\mu\text{-}O)_2$ is shown for comparison in Figure 3c. In comparison to $(EDTA)_2Tc_2(\mu\text{-}O)_2$, the soluble radiolysis product has a longer Tc-Tc distance of 2.58 Å. The spectra of the soluble radiolysis product are consistent with a molecule having the same $Tc_2(\mu\text{-}O)_2$ core as $(EDTA)_2Tc_2(\mu\text{-}O)_2$, but having different ligands. Since Tc(V) complexes with diolate ligands are stable in strongly alkaline solution,[7] it is possible that the soluble radiolysis products are $(diol)_4Tc_2(\mu\text{-}O)_2$, where diol is $^-OCH_2CH_2O^-$ (ethylene glycol), $(^-O)_2CHCO_2^-$ (glyoxylate), or $(^-O)_2CH_2$ (formaldehyde).

Immobilization of technetium. Initial studies with technetium have focused on the use of hydrophobic supports, particularly commercially available functionalized polystyrene. Adapting literature chemistry, both amine ($-NH_2$) and isocyanato (-NCO) functionalized resins were generated.

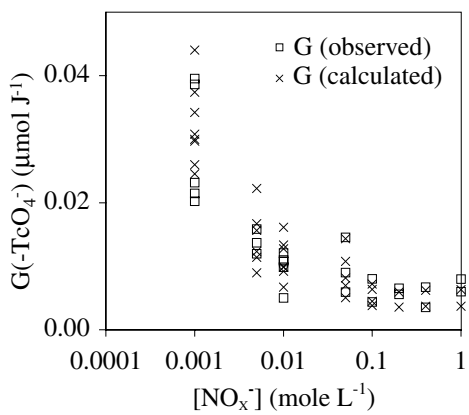

Figure 1: Observed and calculated radiation-chemical yields for the reduction of TcO_4^- in 0.1M (IDA) versus $[NO_3^-]$ and $[NO_2^-]$.

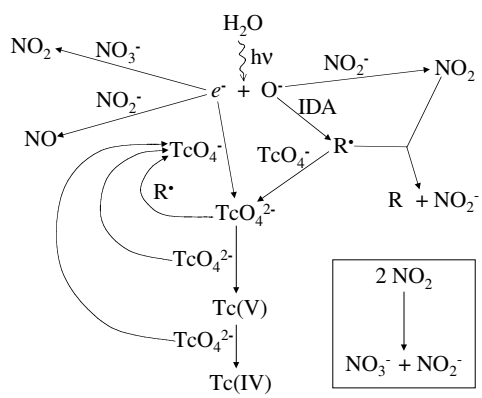

Figure 2: Reaction scheme for calculating the radiation-chemical yields for the reduction of TcO_4^- in solutions of IDA, nitrite, and nitrate.

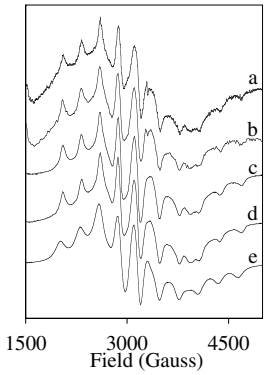

Figure 3. EPR spectra of a) $TcO_2 \bullet xH_2O$, b-d) Insoluble products of radiolysis in citrate, ethanol, and EDTA, respectively, d) simulated spectrum.

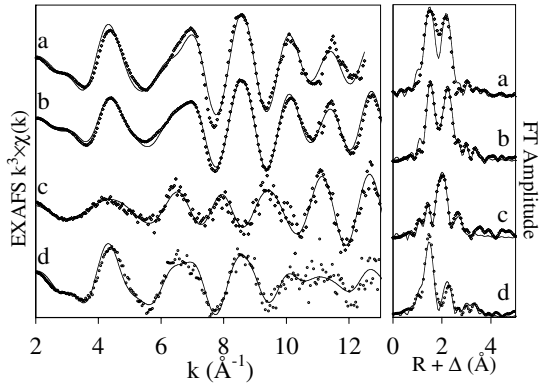

Figure 4. EXAFS spectra (left) and Fourier transforms (right) of a) Insoluble product of radiolysis of TcO_4^- in 2M NaOH and 0.3M EDTA, b) $TcO_2 \bullet xH_2O$, c) $(EDTA)_2Tc_2(\mu\text{-}O)_2$, d) soluble product of radiolysis of TcO_4^- in 2M NaOH and 0.1M glyoxylate.

These resins were found to bind and remove heptavalent technetium complexes ($MeTcO_3$ and Me_3SiTcO_3) readily from nonaqueous media. EXAFS and IR spectral data suggest that while comparable rhenium complexes can undergo reduction upon contacting with the support, technetium is bound as Tc(VII). Leaching experiments were performed in both acidic and basic media (with coadditives to promote swelling of the polymers to minimize phase effects). Minimal leaching into aqueous solution was noted; somewhat higher levels of leaching were observed using organic solvents.

Planned Activities

Solutions containing the soluble radiolysis product will be examined using EXAFS and Raman techniques. Furthermore, we will attempt to crystallographically characterize either the Tc(IV) or Re(IV) complexes. Radiolysis of TcO_4^- in 2M NaOH with added ethanol, nitrate and nitrite will be investigated, and the rate law for radiolysis of TcO_4^- in 2M NaOH with added organics, nitrate and nitrite will be refined. Further studies on technetium immobilization will examine the use of functionalized, water-soluble polymers for binding pertechnetate in aqueous media.

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Interfacial Radiolysis Effects in Tank Waste Speciation

Project ID: 54646

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Research Objective

The intent of this program was to establish an understanding of the role of solid-state radiolysis, secondary electron interactions, charge transfer dynamics and the general effect of heterogeneous solids (interfaces and particulate surface chemistry) on tank waste radiation processes. Specifically, there was a need to understand the role of interfaces and solids in the generation of noxious gases and the mechanisms of organic compound degradation.

Research Progress and Implications

This report summarizes work after 3 years of a 3-year project.

- The interaction of ionizing radiation with nitrate and nitrite solids can contribute to the production of noxious gases in mixed-waste tanks. Low energy (5-100 eV) electron-beam induced gas generation from $NaNO_3$ surface is examined using laser resonance enhanced multiphoton ionization detection of the neutral desorption products, post irradiation temperature programmed desorption, secondary electron emission microscopy and Auger electron spectroscopy. The damage initially involves destruction of the nitrate group, decay of $\{NO_3^-\}^*$ and production of non-thermal O and NO fragments. At higher electron fluences, thermalized NO and O_2 are also produced supposedly due to unimolecular dissociation of NO_3^*. NO_2 is also detected as a minor product. O_2 gas is found escaping from the irradiated $NaNO_3$ in thermal cycling, and is associated with thermal decomposition of several radiation defects. *These oxidants contribute to the degradation of organic waste constituents but also help initiate the generation of flammable gas.*
- Charge transfer across the silica nanoparticle/water interface was studied by picosecond pulse radiolysis utilizing 20 MeV electrons. For the 7 - 22 nm silica particles studied, essentially all electrons generated in the silica cross the interface and appear as hydrated electrons. Organic molecules (methyl viologen) adsorbed on the silica nanoparticle surface capture these "interfacial" electrons very effectively. For high-level radionuclides stored in suspensions, the presence of particles could promote generation of water radiolysis products (of particular concern is H_2) in the vicinity of the particles. This may increase the probability of retention of products near the particles, e.g., by gas-bubble attachment to the particle, and may lead to safety concerns.
- Radiolytically produced NO_2 is shown as the dominant oxidant, promoting aging of the organic component of the mixed waste. Reactions of model organic complexants with NO_2 in water were studied in detailed. The results show that nitrilotriacetate (NTA) degrades via stepwise dealkylation giving mainly formate, carbonate and oxalate. Formate degrades to carbonate when reacted with NO_2, but at a slower rate. Relative reactivities from competition experiments show NTA> iminodiacetate (IDA)>glycine> formate. The rates of production of carbonate and nitrate ions were measures at different hydroxide ion and NO_2 concentrations. The data from this program have improved a predictive computational model of radiation/thermal organic degradation in mixed tanks.

Planned Activities

This EMSP program will formally conclude at the end of FY2000 and it has branched into several new funded programs: "Effects of Water Radiolysis in Water Cooled Nuclear Reactors" (NERI); "Mechanisms and Kinetics of Organic Aging in High-Level Wastes"(EMSP). Finally, a collaborative effort is underway with theorists at PNNL and NDRL to develop kinetic models by calculating thermochemical properties that are difficult to measure experimentally.

Information Access

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NO_x and Heterogeneity Effects in High Level Waste (HLW)

Project ID: 55229

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Research Objective

We summarize contributions from our EMSP supported research to several field-operations of the Office of Environmental Management (EM). In particular we emphasize its impact on safety programs at the Hanford and other EM sites where storage, maintenance and handling of HLW is a major mission. In recent years we were engaged in coordinated efforts to understand the chemistry initiated by radiation in HLW. Three projects of the EMSP ("The NO_x System in Nuclear Waste," "Mechanisms and Kinetics of Organic Aging in High Level Nuclear Wastes, D. Camaioni – PI" and "Interfacial Radiolysis Effects in Tanks Waste, T. Orlando - PI") were involved in that effort, which included a team at Argonne, later moved to the University of Notre Dame, and two teams at the Pacific Northwest National Laboratory. Much effort was invested in integrating the results of the scientific studies into the engineering operations via coordination meetings and participation in various stages of the resolution of some of the outstanding safety issues at the sites. However, in this Abstract we summarize the effort at Notre Dame.

Two broad issues were identified as bottlenecks in understanding the chemistry in HLW a) the heterogeneity of the systems and b) the relatively poorly understood chemistry of NO_x species (rather than water degradation products).

Research Progress and Implications

As a result of the EMSP projects mentioned above the following advancement were achieved, starting with the NO_x issue:

1. All of the initial water primary products are converted to the NO_2 or NO oxidizing species. The rates of these conversions were quantified and novel routes for the conversions outlined. Redox potentials of the relevant species were measured. 2. The hypothesis that NO_2 is the major oxidant of organic compounds in the HLW was confirmed. Relative rates, and in some cases absolute rates, of the NO_2 radical with organic substrates (mostly chelates and their degradation products) were measured. Mechanisms and rates of the reaction of relevant organic radicals with NO_2, and NO_2- were collected. 3. These quantitative measurements were incorporated into a simplified computer model that describes the radiation-induced chemistry of HLW simulants and their mixtures.

On the heterogeneity issue, the following discoveries can be noted:

1. All electrons that are produced by the radiation in solid (silica) particles, at least up to 22 nm in diameter, escape the solid and appear in the water. Thus small particles (or high porosity and large surface area materials) will not prevent some of the effects of radiation on water. 2. All the holes that are generated in the same solid are trapped in the particles. Oxidative processes may or may not (depending on the trap in the solid) be prevented by the solid particle. 3. Either one of these observations can be manipulated by modifying the surface of the particles. However, merely changing the surface charge will not alter the initial conclusions. 4. The charge separation that occurs across the solid/

water interface, as described above, may lead to back-reactions at later stages of the radiolytic effects. Thus, H2 yields may be modified because of re-oxidation of molecular hydrogen by trapped holes.

Specific technological problems that utilized the scientific knowledge developed here can now be outlined: 1. Quantitative computation of the rate of the degradation of organic compounds in HLW simulants was instrumental in the resolution of the organic tanks issue. 2. The outlined mechanisms, and later quantitative calculation of the rate of hazardous gas generation in simulants, eventually lead to predictive calculations of gas generation in waste tanks. 3. Estimates of the rate of gas generation at the surface of wet solid fissile materials, stored for transportation in sealed canisters, is becoming more realistic.

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

Project ID: 65410

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Dr. Glendon W. Gee, Pacific Northwest National Laboratory
Dr. Scott W. Tyler, Desert Research Institute
Dr. John S. Selker, Oregon State University

Research Objective

The primary objective of this project is to develop a basic understanding of the fate and transport of caustic radioactive brines through the vadose zone. Research is focused primarily on migration of high-level waste leaked from single-shell tanks under environmental conditions, and over temporal and spatial scales relevant to the Hanford Site. Understanding the fate and transport of these wastes through the vadose zone is critical to the development of a framework for evaluating different waste retrieval/ remediation strategies and the associated health risks. The hypothesis underlying this project is that elevated surface tension of the leaked tank wastes will strongly inhibit lateral contaminant spreading, giving rise to narrow fingers of infiltration through the vadose zone. The extent and persistence of these fingers will be enhanced by the water migrating into the saline zone in response to the osmotic potential gradient. To validate this hypothesis, this project combines a series of laboratory, field, and numerical experiments with the following specific objectives:

1. investigate the effect of elevated surface tension of highly saline fluids on wetting front instability, finger formation, and contaminant mobility
2. investigate the conditions under which osmotically driven vapor flux is operative and quantify its impact on plume transport
3. 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.

Previous attempts to predict field-scale contaminant transport through the vadose zone have often neglected driving forces and mechanisms that can lead to non-uniform flow. Nonuniform flow has been shown capable of producing erratic transport patterns and can cause contaminants to bypass much of the unsaturated soil matrix. These processes not only lead to fast transport of contaminants to underlying groundwater, but the resulting lack of interchange between the main soil matrix and the fast pathways reduces the potential for natural attenuation.

Two mechanisms that could strongly influence flow non-uniformity and speed the movement of tank wastes in the vadose zone are 1) wetting front instability, due to the high interfacial energy of the saline waste and 2) osmotically driven vapor fluxes, due to the high ionic strength of the waste. Although wetting front instability has been studied extensively in the laboratory, little is known about the formation and persistence of gravity-driven fingers under hydro-geological conditions characteristic of tank farms. The contribution of gravity-driven unstable flow to vadose zone transport could also be enhanced by the migration of water vapor from the surrounding soil into the saline plume. Studies of osmotically driven vapor flux, which have been mostly limited to agricultural fertilizers, suggest that this mechanism can significantly increase the resident water content of the saline soil zone. This mechanism, when coupled with formation of gravity-driven fingers, has the

potential to significantly increase contaminant migration rates through the vadose zone. Our strategy is to combine innovative laboratory, field, and numerical experiments to identify the conditions under which these mechanisms are active and to quantify the impact of vadose zone transport processes. The product will be a tool that DOE can use to perform more realistic analyses to predict fate and transport of vadose zone contaminants, evaluate different tank waste retrieval strategies and their impact on the vadose zone, and assess the associated health risks.

Research Progress and Implications

This project combines a theoretical, experimental, and numerical approach to developing an understanding of the driving forces and complex mechanisms affecting the migration of caustic, radioactive brines through the vadose zone. The project is divided into three main components: 1) controlled laboratory experiments, 2) controlled field experiments in the 200 Area of the Hanford Site, and 3) numerical modeling studies. Controlled laboratory experiments are being conducted at the Desert Research Institute, Pacific Northwest National Laboratory (PNNL), and Oregon State University (OSU). The numerical component is being performed at PNNL, and the controlled field experiments are being conducted at the Hanford Site. Although the project has been in operation for only six months, progress has been made in each of these areas and is summarized in the following sections.

Controlled Laboratory Experiments

Traditional approaches to interpreting and predicting contaminant transport distributions generally assume ideal properties for water and the water-solid-air interfaces. However, the solute concentrations found in Hanford tank wastes may invalidate this simplification. Density- and osmotically driven flows studied in this project must be coupled with measured fluid and porous media properties. To accommodate this data need, a detailed laboratory analysis of fluid-soil interactions is being conducted to determine the effect of concentration of salt in the imbibing solution, surface tension of imbibing and resident fluids, osmotic potential of imbibing fluid, soil texture, and antecedent moisture content.

Laboratory Analysis of Fluid Transport Properties

To date, work has focused on the design of fluids to mimic the ionic strengths and surface tensions of the Hanford tank fluids. These fluids are to be used in the field experiment phase of the research and will be used in the laboratory on a smaller scale. A review of the literature on these physical properties and the properties of the Hanford tank fluids has been completed to choose appropriate field and laboratory fluids for testing. Increases in surface tension above that of pure water are easily obtained using common salts such as NaCl, $NaNO_3$, and $MgCl_2$. In each of these cases, surface tension may be extended to 10–30% over pure water. In addition, at concentrations required for surface tension augmentation, the fluid ionic strengths and water activity are sufficient to induce steep osmotic gradients between the fluid and vapor phases present in soil water.

To achieve much higher surface tensions than those above, it was determined that adding NaOH would be most appropriate. While such compounds are present in many of the Hanford tank fluids, their chemical and safety attributes are less than desirable. This is especially true for the field setting. The strong base developed with an NaOH solution may be highly reactive in the soils found at Hanford; in particular, reaction of basalt-derived sediments and the fluid phase will result in the release of large volumes of silica. As fluids infiltrate deeper into the profile, the solution pH will decline due to these reactions and silica is likely to then precipitate into the pore spaces, perhaps as amorphous silica. The resulting changes in soil porosity and permeability due to silica translocation could be extreme. Such reactions would significantly confound the objectives of both the field and laboratory analysis of the processes called out in our objectives.

We have concluded that for the field experimental portion, a concentrated $NaNO_3$ solution will be used as the permeant ($\sigma = 87.05$ at 47% by weight). The field experiments will mimic the infiltration of high surface tension, low water activity solutions into typical Hanford sediments with relatively pure water forming the antecedent moisture. Significant degradation reactions are unlikely to occur in the subsurface at the concentrations to be used. In addition, microbial uptake of the NO_3 is unlikely, again due to the high ionic strength of the solution.

In the laboratory, we have developed two procedures. We will conduct water retention and imbibition experiments using Hanford sediments and $NaNO_3$ solutions to confirm behavior in the field. These experiments will look at the effects of surface tension and high ionic strength on water retention and conductivity. To assess the effects of surface tension only on wetting front instability, we have developed an alternative to the concepts of significantly raising the surface tension of the imbibing fluid. We will produce the same net effect, i.e., imbibition of high surface tension fluid into low surface tension fluid, by first wetting the soil samples with a solution of water and 1-butanol, which can dramatically lower the surface tension at very low concentrations (Smith and Gillham 1999). Pure water will then be used as the imbibing fluid. In this manner, we can study the effects of high surface-tension imbibition (pure water) into low surface-tension antecedent moisture (1-butanol). The processes will be identical to those found with Hanford fluids but will be free of geochemical and osmotic effects. Soil core samplers have been prepared for the field to obtain intact core samples at the field site for laboratory analysis. Construction of a surface tension measurement system (Sugden 1922, Maximum Bubble Pressure Method) is under way.

Flow and Transport in Miller Similar Sands

Work at OSU's Flow Visualization Laboratory involves the use of light transmission chambers and digital camera systems to study the migration of dense fluids through well-characterized Miller similar porous sands. This technique provides a powerful system for exploring the effects of the large number of variables that can influence transport behavior.

The project required a post-doctoral fellow to conduct the laboratory and field experiments. Following immediately upon receipt of the grant, advertisements were written for a post-doc with a closing date of December 31, 1998. A short list was developed on January 31, 1999, and full applications and references were received in February. Dr. Noam Weisbrod was selected in March and will begin work on the project on June 1, 1999.

In the interim, tests were conducted with Hanford sediments on light transmission systems. The Hanford sands, being basaltic in nature, are black and have proven not to be amenable to the conventional light transmission method. Over the past months, a variety of techniques have been tried for enhancing the visualization system. It is now apparent that the nature of the Hanford sediments may prove to be a limitation in the use of this technology. This problem will be overcome using blended quartz sands as surrogates to the site sands. These sands have already been painstakingly characterized for hydraulic and chemical properties at OSU. The comparison of flow behavior in the various textural blends will allow discrimination of the controlling flow processes through hydrodynamic scaling and will allow for ready interpretation of results.

Flow and Transport in Hanford Sediments

The main purpose of this component of the project is to obtain a data set from real Hanford soils to complement those obtained from the Miller similar sands. It is unclear to what extent wetted path geometry is influenced by minor soil morphological heterogeneity and how the combined effects of osmotically driven vapor flux will affect transport in real systems. Thus, this task will also seek to measure and compare the effects of the salt concentration, osmotic potential, and surface tension of the infiltrating fluid.

Early tests at the OSU Flow Visualization Laboratory show that the opacity of the Hanford sediments disqualifies the use of light-based flow visualization techniques. Furthermore, this technique is not applicable to the coarser gravel-dominated series of the Hanford Formation (discussed below). Over the past few months, a series of experiments has been conducted with the goal of adapting existing techniques for monitoring controlled flow and transport in these soils at scales relevant to the understanding of finger formation and persistence.

One technique that shows promise is x-ray computed tomography (XRCT), on which testing was initiated in early 1999 at PNNL. In the tests, four columns (15 cm long x 3.8 cm) were packed with soil. One-half of the columns were packed at air-dry moisture content while the other half was packed 10% by volume of water. Each column received a 5-mL application of saturated NaI solution (1.4 g L^{-1}), to simulate a dense saline fluid, and was monitored over time by XRCT to evaluate its

efficacy for monitoring flow in opaque soils and identifying the conditions under which gravity-driven flow instability occurred.

Figure 1 shows an example of a transverse 2-dimensional image from the opaque basaltic sand. The volume displayed is representative of the attenuation values in gray scale. These attenuation values, corresponding to the density within the volume, display rocks or dense material as white and air as black. Not only is the pore space, consisting of various channels and voids, clearly seen in these images, but the plume of NaI is also quite clear. Finger formation is clearly seen in Figure 1a, while the solute front is somewhat more diffused in the wet soil (Figure 1b). Finger formation and persistence in the wetter soil may have been overcome by the heterogeneities caused by packing.

Figure 2 shows cross-sectional views of the same two columns at about 4 cm from the surface. In Figure 2a, a compact, well-defined outline of the NaI plume is clearly seen as a denser (white) zone. In the wetter soil, the solute front spread laterally along the stratification, essentially wetting most of the pore space, hence the more widely distributed, high-density zones (Figure 2b).

These images clearly show that the XRCT technique has potential for monitoring finger formation and persistence in opaque soils. These micro-lysimeter studies are being used to provide information on the initiation and persistence of fingers over a range of conditions. A major advantage of the XRCT system is that the transverse images can be assembled and rendered as 3-dimensional images from which the multidimensional features of fingers can be studied. Thus far, studies of fingers have been limited to thin, 2-dimensional columns that can be monitored using light-based transmission techniques. The results of these experiments will be used as a basis to design an intermediate scale (2 m x 1 m flow cell) laboratory experiment in which fingering phenomena will be monitored, including a fully automated dual-energy gamma radiation system and time-domain reflectometry (TDR) systems.

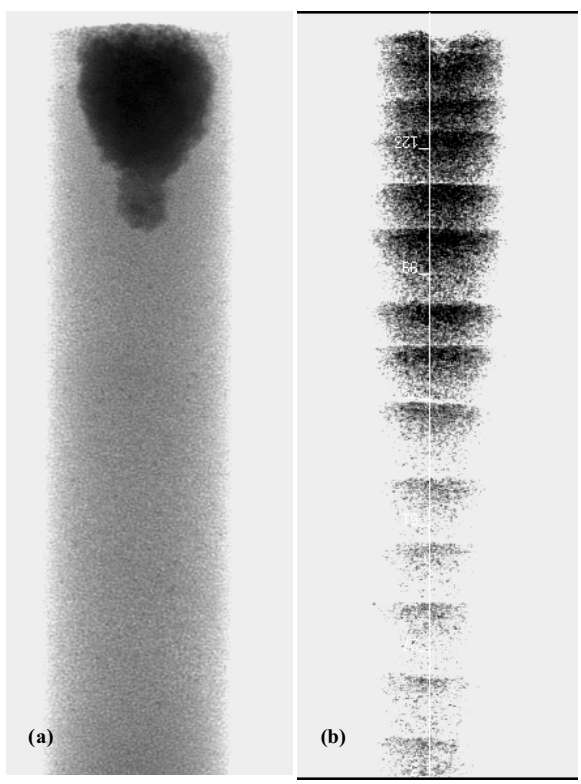

Figure 1. Sagittal CT Image Displaying Pore Space and Distribution of a Dense NaI Plume After 24 Hours of Redistribution (a) initially air-dry soil, (b) soil wet to a water content of 0.10 m^3 m^{-3}

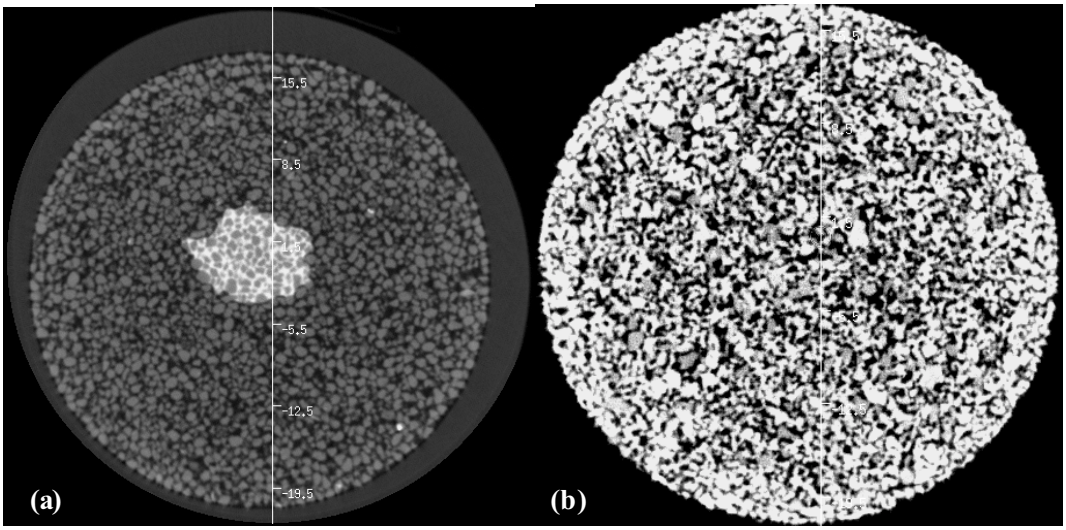

Figure 2. Transverse XRCT Image Displaying Pore Space and Distribution of a Dense NaI Plume After 24 Hours of Redistribution (a) the compact finger is maintained in the initially air-dry soil, (b) finger is dispersed due to layering in soil initially wet to a water content of 0.10 m^3 m^{-3}

Field Experiments

The field experiments are intended to explore saline plume transport at two time scales, a reflection of the different time scales at which initial imbibition and vapor migration processes proceed. The objectives of the field component of this project are to

1. identify the degree to which field conditions mimic the flow processes observed in the laboratory
2. provide a validation data set to establish the degree to which our conceptual models, embodied in a numerical simulator, explain the observed field behavior.

We toured the Hanford Site in the fall of 1998 to investigate possible field sites. Based on the findings of the tour and subsequent discussions, planning and preparation for field activities were started. Two sites were selected to represent the extreme in porous media properties representative of the Hanford tank farms and the paperwork started to obtain the necessary permits. The permits were obtained in May 1999, and instrumentation has commenced.

Most of the tanks at Hanford were placed in the upper Hanford formation, and much of the site outside of the tank farms is covered with a 1–2-m layer of Holocene eolian deposits. Therefore, before the field experiments are conducted, the top 1–2-m of deposits had to be removed to expose the Hanford formation. The first site is located near the 200 West Area of the Hanford Site and is representative of the gravel-dominated Hanford formation (Figure 3a), the unit in which most of the waste resides.

The second site is located in the 200 East Area and is representative of the sand-dominated Hanford formation (Figure 3b). Both sites have been excavated in preparation for instrumentation and conducts the characterization and long-term plume migration studies.

The field experiment requires a 48 probe, multiplexed five-level TDR system. The entire system is designed to be fully automated with remote download capacity via cellular phone. The system will document the movement of water and salt along the flow paths of six separate plumes on a twice-daily basis. All system components have been acquired and the system is largely assembled (Figure 4a). The system is to be installed in the field in early June 1999. Each probe has been calibrated before installation (Figure 4b shows the method outside of calibration fixture).

Numerical Studies

Numerical modeling of gravity-driven flow instabilities using a continuum approach has only recently been successful through adjustment of the upstream weighting coefficient of permeability in a finite

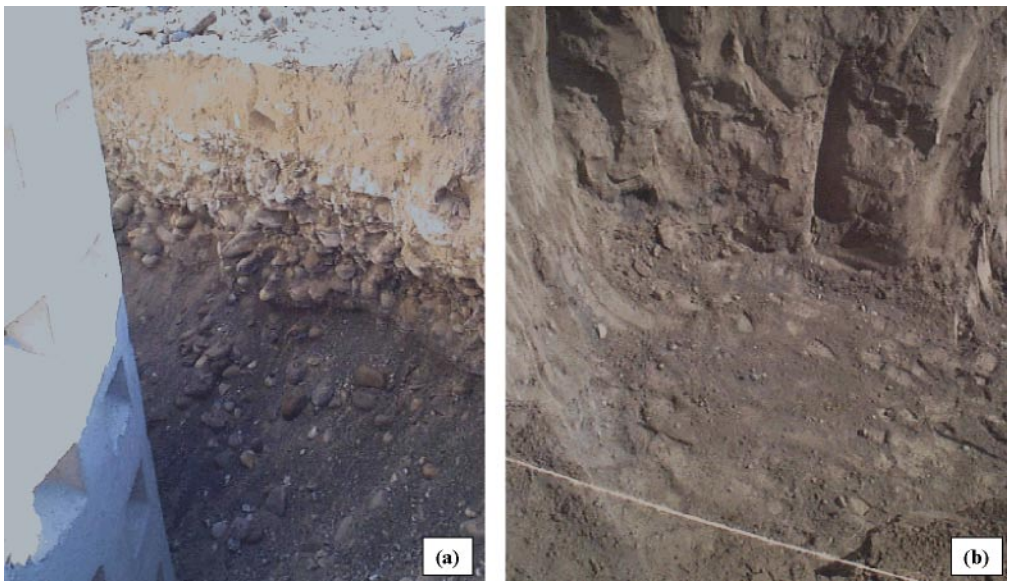

Figure 3. Photograph of (a) Typical Soil Profile in the Upper Hanford Formation at the 200 West Area Site and (b) the Sand-Dominated Site in the 200 East Area

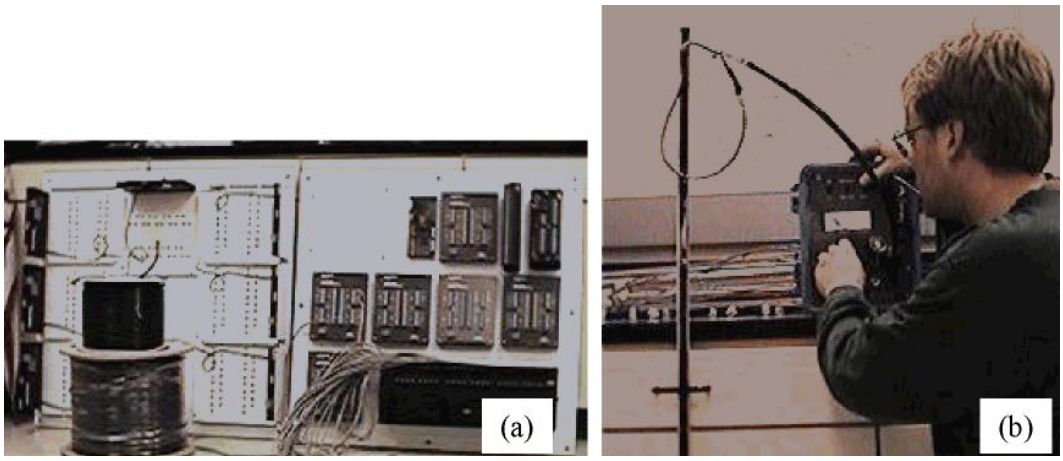

Figure 4. Photograph of Moisture Monitoring System for the Field Experiment. Each probe has been calibrated before installation (a) assembly of system, (b) system outside of calibration fixture

element model (Nieber 1996). It has also been suggested that the mechanism for the initial formation of flow instabilities and their persistence is best described in terms of the water retention _(_) and hydraulic conductivity K(_) relations for the given soil. Although the nature of the problem means that the solutions to the flow and transport equations may possess highly localized properties in both space and time, application of these techniques has been limited to relatively small domains (≤2 m x 2 m) with uniform 2-dimensional grids.

It has become increasingly clear that multigrid methods represent the most efficient approach for iteratively solving the large system of algebraic equations that arise from large-scale numerical simulations modeled by partial differential equations (Bramble et al. 1996). To scale the highly localized behavior of fine-scale fingering generated by heterogeneous porous media or flow instabilities up to computational and field scales, work has started on techniques for obtaining effective parameters for coarse-grid models that are consistent with fine-grid simulations. Over the past months, work has been ongoing to modify the multidimensional Subsurface Transport Over Multiple Phases (STOMP) computer software program to incorporate an adaptive mesh refinement. The approach is to use

adaptive mesh refinement to cluster grid points in regions where they are most needed, e.g., around a developing flow instability or other regions where the solution has steep gradients. This strategy is being developed for both temporal and spatial refinements on Cartesian grids and will ultimately take advantage of the vectorization of the STOMP simulator.

The time-stepping scheme is an integral part of the adaptive gridding solution technique; the first step was to implement a second-order, two-step implicit backward differentiation formula (BDF) method for solving the differential-algebraic equations into STOMP. A series of tests to compare the default Euler scheme in STOMP with the new BDF scheme has been successful. In a test involving a one-dimensional infiltration problem, the Euler scheme executed the problem in 65 time steps with one convergence failure, while the BDF scheme executed the same problem in 49 time steps with no convergence failures and produced essentially the same results. Schemes to allow description of a variable upstream weighting parameter and definition of the hysteretic water retention and hydraulic conductivity models, critical to modeling flow instability, have also been implemented.

Planned Activities

During the next year, work will continue at the Desert Research Institute to obtain water retention and unsaturated hydraulic conductivity measurements on samples recovered from the field beginning in the summer of 1999. Pure water, $NaNO_3$, and 1-butanol solutions will be used. Following completion of this characterization, imbibition experiments will be conducted using both pure water imbibing into pure water (as a control) and 1-butanol imbibing into pure water. It is anticipated that these experiments will begin at the end of summer 1999 and will be completed by winter 1999-2000.

Work at the OSU Flow Visualization Laboratory will continue to study the effects of heterogeneity of finger formation and persistence using simple horizontally layered systems of pairs of Miller similar sands. These experiments will attempt to determine the ability of the surface tension effects to overcome the attenuating effect on fingered flow observed in naturally occurring layered systems. These tests are expected to start in July 1999.

In the PNNL-controlled laboratory studies, work will proceed on calibration of the XRCT system to permit conversation of attenuation values into soil water content/solute concentration. We will further investigate the conditions that lead to finger formation and the characteristics that influence persistence during wetting and drying cycles. The medium-scale flow experiment will begin in late summer 1999.

Starting in June 1999, and before the field-scale experiments at the two sites begin, detailed hydraulic and stratigraphic analysis will be performed. Based on these analyses, experimental design parameters (e.g., water application rates, sensor location, sampling frequency) will be developed using predictive models. Site instrumentation should be completed by the end of July 1999, after which the long-term plume migration studies should begin. Following the long-term plume migration experiments, the plots will be excavated to further investigate the tracer transport as well as to characterize the hydraulic properties directly beneath the field site.

Theoretical analysis and model simulations of pure water entering initially dry soils show that finger formation results from hysteresis in the water retention function and that the characteristics of the finger depends on the shape of the main imbibition and drainage branches. During the next year, work will continue to incorporate the effects of surface tension inferred from the laboratory water retention and unsaturated hydraulic conductivity measurements using tank waste simulants. Work will also continue toward the implementation of the adaptive mesh refinement strategy. Numerical experiments will continue with the goal of elucidating the regime that leads to the onset of fingering and to determine how finger characteristics are influenced by vapor flux in response to osmotic potential gradients.

Information Access

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Imaging and Characterizing the Waste Materials Inside an Underground Storage Tank Using Seismic Normal Modes

Project ID: 55141

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Roger M. Turpening, Massachusetts Institute of Technology

Executive Summary

Observing and sampling the contents of Hanford's underground storage tanks has always been a difficult problem. Although various types of coring and sampling devices exist, one sampling operation is time-consuming, difficult, and even at its best results in only a point measurement of a large volume. Furthermore, at various times in the past it has been especially important to know whether an entire gas layer or volume existed in the waste of a given tank.

Many techniques exist in the hydrocarbon industry for imaging the earth, but it is not easy to employ them in a tank. The best imaging methods require two boreholes in a tank, and indeed the MIT Earth Resources Laboratory (ERL) was successful in implementing such a method in tank 114 TX using its two liquid observation wells (LOWs). However, all other tanks have only one LOW, which controlled the direction of the work reported here.

Given the importance of knowing as much as possible about the contents of a specific tank and given that the tank will have only one LOW, we examined the information that could be obtained from the natural seismic vibrations of a tank as a whole, that is, the normal modes of that tank. As in the case of a bell, the natural vibration, or normal modes, of a tank depend on many things, including the construction of the tank, the kinds of waste materials in the tank, the amount of each material in the tank, and where the energy is placed that excites the vibrations (i.e., where you will "hit" the tank).

The nature of natural vibrations is not affected by where one "listens" to them, although one might miss one or several "overtones" if the recording instruments are in poor locations. Throughout this research it was assumed that the "listening devices" would be hydrophones and they would be deployed in the one LOW that exists in every tank. It was also assumed that in any future deployment of this method, the seismic energy to excite the natural vibrations would be a small vibrator placed outside a tank and on the earth's surface. The research reported here involves the theoretical computations and small physical model studies needed to understand these normal modes.

We used layered models, both numerically and physically, of wastes in a tank. These restrictions in no way reduced the value of the research. We were seeking a measure of the sensitivity of the normal modes to the kinds and volumes of wastes in a tank.

The nature of a normal mode of vibration can be given by its frequency and amplitude. For any given frequency, the amplitude of vibration can be given as a function of position in and around the tank. Since we assumed that one would be "listening" to a tank from locations along a LOW, we show our computed amplitudes as a function of position inside and around the tank, and in the case of our physical models we display the observations along various lines inside the tank model. This allowed us to see the complex geometry of each mode of oscillation as a function of increasing frequency.

Several different liquids (oil, water, heavy mud, etc.) were used both numerically and physically. We observed strong differences in location of the spectral peaks for layers (of various thicknesses) of liquids that differed only slightly in density. We also changed the total volume of wastes in a given tank.

We scaled our results up to represent full-sized Hanford tanks and found that the spectral band of the normal modes was in a range of frequency (tens to hundreds of Hertz) that is easy to generate and record in the field. Thus a technique that, with a minimum of intrusion, can discriminate various total volumes of layered wastes, stands ready for field testing should that be desired.

Relevance, Impact and Technology Transfer

This research project produced knowledge that can be used to make rapid estimates of the nature of wastes in underground tanks. These estimates can be made using small seismic sources and receivers on the earth's surface outside the tank. This knowledge is valuable if an early selection must be made between various kinds of sampling, pumping, sluicing, etc. hardware. If such hardware performs properly no matter the nature of the waste, then even an estimate of the nature of the waste is not needed.

This project was a perfect example of the application of an old fundamental technique that has been used in many engineering and scientific fields, to a new, important, and specific problem. The earth sciences has used normal mode studies for decades to estimate the properties of the earth as a whole. Here, it was scaled down to a single underground tank application.

Phase Chemistry of Tank Sludge Residual Components

Project ID: 60403

James L. Krumhansl, Sandia National Laboratories

Kathryn L. Nagy, University of Colorado
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Patrick V. Brady, Sandia National Laboratories
Bradely Wakoff, University of Colorado

Research Objective

In the late 1940s, the Hanford nuclear facility in eastern Washington began reprocessing spent nuclear fuel. This treatment reclaimed usable U and Pu, but left behind large volumes of high level radioactive waste (HLW). A change in U.S. nuclear policy terminated reprocessing in the 1980s, but the HLW produced in the intervening decades remains stored in underground, steel-lined, concrete tanks. It is estimated that tank leaks have released about 1 million curies of radiation to the ambient Hanford soils. SX tank farm remediation is scheduled to begin in 2004, though the prohibitive cost of sampling and handling HLW has precluded direct detailed analysis of the chemical state of waste in the tanks. Technetium-99 (^{99}Tc) is a long-lived fission product of U present in significant concentrations in Hanford waste. ^{99}Tc is a particular concern in tank remediation because of its high solubility at the Eh-pH conditions present in both the tank waste and the ambient Hanford soils. An understanding of the solid phase chemistry of the HLW stored in the Hanford tanks and the fate of ^{99}Tc within these wastes is needed to initiate remediation. The Hanford HLW is compositionally complex and variable; therefore, we are examining experimentally the aging dynamics of simplified systems whose bulk chemistry approximates that of the tank sludges. Results will provide a baseline for the evolution of the dominant solid phases and their role in separating ^{99}Tc from the solution phase.

About four or five distinct reprocessing technologies were used at various times in Hanford's history. After removing U and Pu (or later ^{137}Cs and ^{90}Sr), the strongly acidic HLW was "neutralized" to high pH (>13) and stored in steel-lined tanks. High pH was necessary to prevent tank corrosion. While each technology produced chemically distinct waste, all wastes were similar in that they were high pH, concentrated, aqueous solutions. Dominant dissolved metals were Fe and/or Al, usually followed by Ni, Mn, or Cr. In an effort to reduce waste volume, many of the wastes were placed in evaporators or allowed to "self-boil" from the heat produced by their own radioactive decay. Consequently, today's HLW has been aging at temperatures ranging from 20º to 160ºC.

Previous studies of synthetic HLW sludge analogues have varied in their exact synthesis procedures and recipes, although each involved "neutralization" of acidic nitrate salt solutions by concentrated NaOH. Some recipes included small amounts of Si, SO_4^{2-}, CO_3^{2-}, and other minor chemical components in the Hanford sludges. The work being conducted at the University of Colorado differs from previous studies and from parallel current investigations at Sandia National Laboratories in the simplicity of the synthetic sludge we are investigating. We are emphasizing the dominant role of Fe and Al, and secondarily, the effects of Ni and Si on the aging kinetics of the solid phases in the sludge. We are also investigating the uptake of rhenium (in the form of ReO_4^-) as an analogue for the soluble form of ^{99}Tc, in the solids vs. the solutions.

Research Progress and Implications

At the University of Colorado, we are in the second year of investigating the aging of simplified sludge compositions (Wakoff and Nagy, 1999). Iron and aluminum comprise the bulk of most HLW

sludges at Hanford; therefore, low Al/Fe sludges are synthesized to approximate Bismuth Phosphate and PUREX wastes, whereas high Al/Fe sludges simulate REDOX waste. The behavior of rhenium as an analogue for technetium (^{99}Tc) in the aging sludges is also being monitored. Experimental samples are prepared as acidic Fe(III)-Al nitrate solutions and then "neutralized" at room temperature to pHs of 13.1-13.7. These samples are aged in a water bath at 90ºC for three months. Solids and solutions are fully characterized at the ends of the experiments by X-ray diffraction, atomic force microscopy (for crystallite morphology), and specific surface area; and, by UV-Vis spectroscopy (Fe and Al), ICP-MS (Re), and pH measurement, respectively. Transformation of solids from amorphous precipitates to crystalline materials (hematite, goethite, bayerite, and gibbsite depending on initial solution composition) is complete after only 120 hours. Aging has been investigated in the presence and absence of 40 ppm Re (as perrhenate: ReO_4^-). While Re oxides are expected to be fully soluble at the pH/Eh conditions of the experimental solutions, the similarities (size, charge, stereochemistry) among the monovalent aqueous anions of Re, Al, and Fe suggest that perrhenate may interact strongly with precipitating metal-oxyhydroxides. Differences in transformation rates of the solids have been observed in both the low and high Al/Fe systems when Re is present. Also, the low Al system solids retain more Re with aging time than the high Al solids, although the concentrations are relatively small at ~ 10-100 ppb Re. Partition coefficients of Re between solid and solution are being determined as a function of aging time.

In a related investigation we have used atomic force microscopy coupled with solution sorption experiments and EXAFS spectroscopy to determine the role of Fe-oxyhydroxide mineral (goethite and lepidocrocite) surfaces in controlling sorption of a divalent cation, Cd^{2+} (Manceau et al., 2000). Such work is significant for understanding sorption of Cs^+ or Sr^{2+} onto Fe-oxyhydroxides in tank sludges and in groundwater/sediment systems such as at Hanford in the vadose zone or the Savannah River site.

Planned Activities

Experiments in progress include those in which Ni and Si have been added as solution components. Ni may aid the formation of a layered-double hydroxide phase, which could incorporate perrhenate along with NO_3^- and CO_3^{2-} in the anionic interlayer of this phase's structure. Silicon is known to inhibit the transformation rates of Fe oxyhydroxides, which may also contribute to higher Re partition coefficients into the solids with aging, primarily due to the higher surface area and amorphous nature of the initial Fe-phase that forms, ferrihydrite.

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Phase Chemistry of Tank Sludge Residual Components

Project ID: 60403a

James L. Krumhansl, Sandia National Laboratories

Research Objectives and Problem Statement

Both the Hanford and Savannah River Sites have high level nuclear waste storage tanks that will eventually be decommissioned. Sludges adhering to the interior surfaces of tanks may eventually contaminate nearby ground waters. To assess the impact of such leakage it is necessary to quantify radionuclide release rates from these sludges. The use of actual sludges for such determinations is both difficult and expensive since handling of such materials must involve working in high-radiation environments. The overall objective of this project is to develop quantitative radionuclide release models for sludges based on non-hazardous analogues.

To achieve this objective will require achieving three scientific goals:

1. Identify and synthesize the principal sludge phases resulting from the major fuel reprocessing methodologies;
2. Compare synthetic and artificial sludge phases to assure that appropriate materials are used in later tests;
3. Develop models and experimental tests to quantify the retention and release of radionuclides by the principal sludge phases as the geochemical environment shifts from what exists today in tanks to what would be expected as the pore fluid chemistry approaches that of normal groundwaters (e.g. pH and ionic strength fall while carbonate/bicarbonate rise).

The general relevancy of these goals to DOE is illustrated by a recent needs statement originated by Hanford site managers:

"Remediation and closure of high-level waste tanks at Hanford will leave residual solids that are estimated to be one of the major long-term radionuclide sources into underlying vadose zone sediments. However, the actual release rate of technetium, selenium and uranium (the major predicted dose contributors from the residuals is essentially unknown. A fundamental understanding of the true radionuclide source-term from the residuals is needed to base sound cost/benefit/risk decisions regarding the extent of waste removal actually required from the tanks to meet site-wide groundwater protection standards [DE/RL-98-01, Rev2, RL-WTO68]"

The relevancy of the programmatic decision to pay particular attention to Tc is supported by a needs statement originated at Savannah River:

"A better understanding is needed of the chemistry of technetium under the conditions of waste removal and under the conditions after tank closure. This better understanding will provide a tool for estimating the Tc-99 concentrations in waste tanks when waste removal is being planned, and will reduce the conservatism of Tc-99 modeling……

An understanding of the chemistry of technetium is desired that would allow confident planning of waste removal and closure from HLW tanks at SRS and other DOE sites. Also, if specific compounds are identified that are precipitating or absorbent Tc-99, it may be possible to identify strategies (such as special cleaning agents) to enhance Tc-99 removal. A better understanding of the chemistry would:

Improve the planning of the tank closure process at SRS and other DOE sites;

Potentially improve the schedule or reduce the cost of tank closure;

Potentially reduce the number of samples that would be needed to develop a credible estimate of the tank inventory. If the chemistry is not well known, then large numbers of samples might be needed to cover any unidentified variability. [SR99-2051]"

Research Progress and Implications

In this, the third of three years of funding we have focused on characterizing the radionuclide retention and release characteristics of sludges. Work at the University of Colorado has focused on the Al-Fe-OH system. Iron and aluminum comprise the bulk of most HLW sludges at Hanford; therefore, low Al/Fe sludges are synthesized to approximate Bismuth Phosphate and PUREX wastes, whereas high Al/Fe sludges simulate REDOX waste. The behavior of rhenium as an analogue for technetium (^{99}Tc) in the aging sludges is also being monitored. Experimental samples are prepared as acidic Fe(III)-Al nitrate solutions and then "neutralized" at room temperature to pHs of 13.1-13.7. These samples are aged in a water bath at 90ºC for three months. Solids and solutions are fully characterized at the ends of the experiments by X-ray diffraction, atomic force microscopy (for crystallite morphology), and specific surface area; and, by UV-Vis spectroscopy (Fe and Al), ICP-MS (Re), and pH measurement, respectively. Transformation of solids from amorphous precipitates to crystalline materials (hematite, goethite, bayerite, and gibbsite depending on initial solution composition) is complete after only 120 hours. Aging has been investigated in the presence and absence of 40 ppm Re (as perrhenate: ReO_4^-). While Re oxides are expected to be fully soluble at the pH/Eh conditions of the experimental solutions, the similarities (size, charge, stereochemistry) among the monovalent aqueous anions of Re, Al, and Fe suggest that perrhenate may interact strongly with precipitating metal-oxyhydroxides. Differences in transformation rates of the solids have been observed in both the low and high Al/Fe systems when Re is present. Also, the low Al system solids retain more Re with aging time than the high Al solids, although the concentrations are relatively small at ~ 10-100 ppb Re. Partition coefficients of Re between solid and solution are being determined as a function of aging time. Planned experiments include adding Ni and Si as solution components. The formation of a layered-double hydroxide phase is possible in the presence of Ni. Such a phase has an anionic interlayer to balance excess positive charge in the octahedral sheets. Perrhenate could reside in the interlayer, resulting in a higher solid/liquid Re partition coefficient. Silicon is known to inhibit the transformation rates of Fe oxyhydroxides, which may also contribute to higher Re partition coefficients with aging. The presence of Si could also possibly lead to the formation of a Ni-aluminosilicate clay.

The Sandia-PNNL part of the team has continued to develop an understanding of the behavior of more complex sludges resembling mixes such as would be found in tank bottoms. In particular, experimental studies were undertaken to quantify the uptake and release of RCRA metals and radionuclide surrogates. Table 1 summarizes levels of dissolved constituents measured experimentally in fresh waters that were exposed to synthetic sludges. These concentrations are similar to what might be expected after groundwater gained access to a tank that had been decommissioned using a grout fill. Note: Re and Se levels are quite low. However post-test analyses of the solid sludges revealed that these low values reflect the loss of these elements during the washes that preceded the equilibration experiment summarized in Table 1. Work also continues on apatite dissolution rates because it is becoming apparent that this phase may be a major trace component sink in some sludges.

Table 1 – Analyzed aqueous concentrations leached from sludges at low ionic strengths (PPB)

Process	$BiPO_4$	TBP	REDOX	PUREX-Al	PUREX-Zr
Al/Fe -molar	2.0	0	9.1	2.9	0
Co	0.3	1.5	>0.2	0.4	>0.2
Sr	0.8	4.9	36.4	0.5	760
Cd	>0.3	3.1	>0.3	>0.4	>0.3
Ba	0.4	2.1	1.6	0.3	92
Nd	0.4	7.4	>0.2	0.4	<0.2
Pb	0.2	1.7	>0.2	0.4	>0.2
Se	>4.5	>4.5	5.7	39.4	>4.5
Re	2.2	0.2	2.8	12.9	1.0
Cs	13.9	7.5	24.9	26.3	1.9
pH	9.6	8.4	10.0	10.0	7.6

Future Research Plans

This is the last year of the grant and the remaining time will be spent on finishing experiments already in progress and on final report preparation. A renewal is being prepared and seeks funding in the following areas:

(1) Continued studies on the retention of ReO_4^- by mixed Al-Fe hydrous oxides;
(2) Evaluating the impact of organic components in the waste both on the phase chemistry of sludge precipitates and on the release of radionculide surrogates;
(3) Evaluating the impact of drying and high temperature aging on sludge chemistry, and
(4) Developing a sorption/desorption database for AlOOH similar to the database which has provided so many geochemical insights for FeOOH.

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Quantifying Silica Reactivity in Subsurface Environments: Reaction Affinity and Solute Matrix Controls on Quartz and SiO_2 Glass Dissolution Kinetics

Project ID: 55042

Patricia M. Dove, Georgia Institute of Technology

Research Objective

Our goal is to develop a quantitative and mechanistic understanding of amorphous silica, SiO_2(am), dissolution kinetics in aqueous solutions. A knowledge of fundamental controls on the reactivity of simple Si—O bonded phases is the baseline of behavior for understanding highly complex silica phases. In the Earth, silicate minerals comprise >70% of the crust and dominate virtually every subsurface system. More importantly for the objectives of this EMSP project, the silicates are important because compositionally complex glasses will become the front line of defense in containing radioactive wastes in the nation's long term and interim storage strategies. To date, the behavior of SiO_2(am) is largely inferred from studies of the better known crystalline polymorphs (e.g. alpha-quartz). In the first step towards constructing a general model for amorphous silica reactivity in the complex fluid compositions of natural waters, we are determining the dissolution behavior as a function of temperature, solution pH and cation concentration. With these data we are determining relationships between SiO_2 glass structure and dissolution rates in aqueous solutions, as described below.

Research Progress and Implications

Interactions with Users: Tank Focus Area and Workshop Meetings

The 1998 EMSP conference in Chicago was an important meeting for our project. The symposium, enabled P.I. Dove to establish valuable contacts with focus area 'users' having specific needs for the findings of our EMSP project related to the urgency of problems in the Tank Focus Area (TFA). Since 1998, our working relations have developed through interactions with TFA scientists and engineers on the problems of waste glass properties. Dove presented the results of EMSP research findings to a TFA subgroup at a Product Acceptance Workshop held in Salt Lake City during December 1998. Travel costs to this workshop were paid from EMSP research funds. In January 2000, Dove attended a similar meeting in Atlanta with participants from PNNL, SRL and BNF to discuss new issues and make another level of decisions on the Product Acceptance goals.

Our current EMSP-funded research has interfaced well with the ongoing glass corrosion studies in the Applied Geochemistry Group at PNNL (contacts: Dr. R. Holdren and Dr. P. McGrail). Shortly after the Chicago conference, our EMSP-funded Postdoc, Dr. Jonathan Icenhower was hired by the same PNNL group. Icenhower brings his experience in silica-water reactivity and the experimental expertise in mineral-water reaction kinetics. With the Icenhower move from postdoc to a staff scientist position at PNNL, our EM project facilitated information transfer from the 'university to user' environment. Similarly, one of our EMSP M.S. students, Mr. Troy Lorier, will be visiting Savannah River Laboratory to discuss a possible position in the glass group (contact: Dr. Bill Holtzscheiter). His thesis research on silica geochemistry meshes with on-going efforts at SRL. In short, our current EMSP project has gone well beyond the strictly academic goals of producing high quality scientific knowledge to establish connections with actual users and produce new talent for the waste immobilization effort.

EMSP 96-10 Project Highlights

This section is intended to highlight the scope of findings made to-date on the current project.

The dissolution kinetics of amorphous silica into sodium chloride solutions: Effects of temperature and ionic strength. **(Icenhower and Dove, in press, *Geochim. Cosmochim. Acta*).** The kinetics of amorphous silica, SiO_2 (am), dissolution was determined in deionized water (DIW) and NaCl solutions at temperatures that span 40-290°C. The model is carefully underpinned with experimental data from our laboratory and assesses all of the published amorphous silica data to produce a critically evaluated comprehensive model. Using two sources of pure SiO_2 glass (fused purified quartz and pyrolyzed $SiCl_4$), dissolution rates were measured in our lab by applying three types of reactor systems to assess kinetic behavior over the full temperature range. Dissolution rates of the two materials are similar within experimental error. Absolute rates of amorphous silica dissolution exhibit an experimental activation energy, $E_{a,xp}$, of 82.4±3.0 and 78.9±1.8 kJ mol^{-1} for the fused quartz and pyrolyzed silica, respectively **(Fig 1)**. These values are similar to each other and to estimates for quartz within experimental errors. Absolute dissolution rates of the amorphous silica in DIW are ~10X faster compared to quartz **(Fig 2a,b)**. Amorphous silica dissolution rates in near-neutral pH solutions are strongly dependent upon the concentration of NaCl such that 0.05 molal sodium ion enhances rates by 30X compared to deionized water. Results of this study show that NaCl can greatly modify the reactivity of amorphous silica.

The findings step toward the larger goal of understanding silica polymorph reactivity in the complex fluid compositions of natural systems. Recent findings that quantify the effects of dissolved solutes on quartz dissolution rates allow us to suggest that other major solutes found in natural waters will also enhance the dissolution rates of amorphous silica in a systematic and predictable manner. Continuing work towards a comprehensive model of silica reactivity will be able to assess these effects.

Fig. 1 a,b

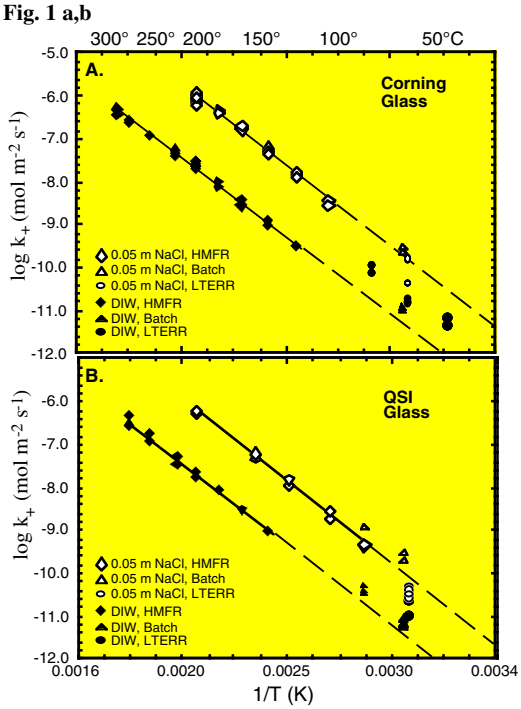
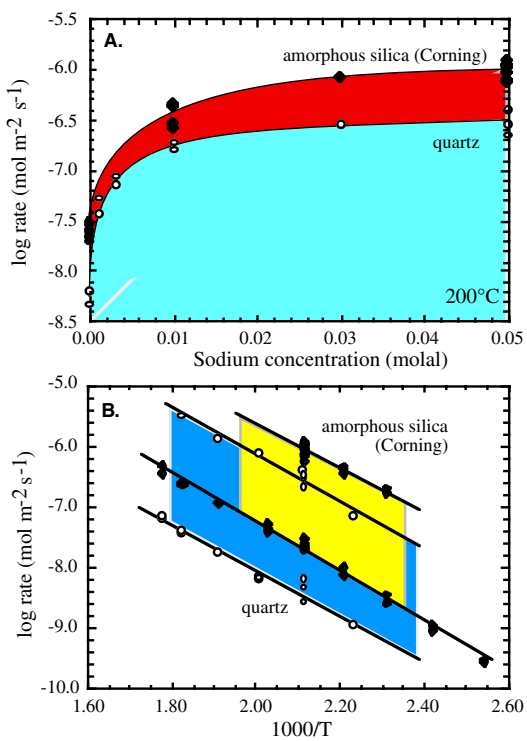


Fig. 2 a,b.



Dissolution kinetics of quartz in aqueous mixed cation solutions. **(Dove, 1999, *Geochim. Cosmochim. Acta*).** The dissolution kinetics of quartz is quantified in dilute mixtures of magnesium, calcium, barium and sodium chloride salts in near-neutral pH solutions over the temperature range of 175 to 295°C. Measurements using single salt solutions show that the rate-enhancing effects increase in the order: $Mg^{2+} < Ca^{2+} = Na^{+} < Ba^{2+}$ **(Fig 3)**. Barium ion increases dissolution rates by 114X compared to new, slower rates found for deionized water ($10^{-8.11}$) at 200°C. Experimental activation energies, E_{xp}, measured for each salt solution are similar within experimental errors **(Fig 4)**. In solution mixtures of two salts, dissolution rates are a nonlinear combination of the bulk concentrations of cations in solution such that rates are limited by the cation with the *smallest* rate-enhancing effect. That is, a small fraction of magnesium ion in the mixture limits the net dissolution rate to an extent disproportionate to its bulk concentration. A comparison of **Fig. 5** with **Fig 6** shows that this behavior is more pronounced for salt mixtures of 2^{+}:1^{+} cations (i.e. Mg^{2+} and Na^{+}) than 2^{+}:2^{+} cations (i.e. Mg^{2+} and Ba^{2+} or Ca^{2+}).

The behavior observed in salt mixtures is quantified by an empirical expression based upon a competitive cation-surface interaction model. The kinetic model assumes that salt-enhanced dissolution rates are determined by the intrinsic ability of each type of cation, i, to enhance rates ($k_{mx,i}$) and their concentration(s) at the surface ($K_{ad,i}$). Estimates of these parameters are obtained by fitting the model to data from the rate versus concentration experiments conducted in single salt solutions. The resulting kinetic expression gives good predictions of rates measured in salt mixtures and is consistent with previous models of cation-enhanced dissolution kinetics of quartz. The model predicts that magnesium and calcium have greater roles in regulating quartz dissolution rates despite lower concentrations in natural waters than sodium and potassium because of their larger surface interaction strengths.

Fig. 3 Comparison of IIA and IA cation solutes on quartz dissolution rate.

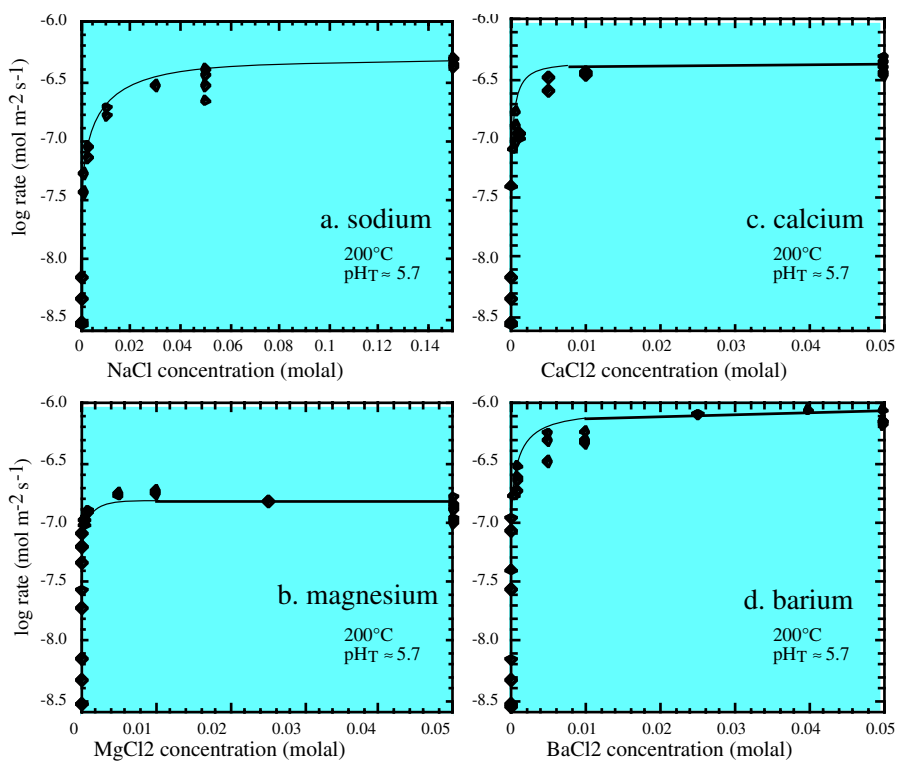


Fig. 4 Temperature dependence of quartz dissolution in deionized water and 0.05 M chloride salts.

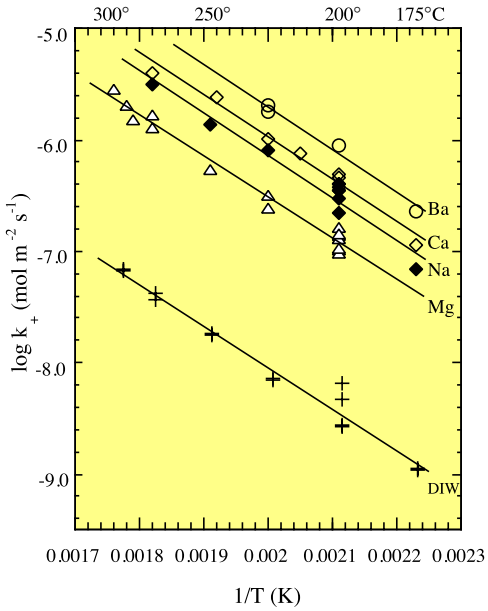


Fig. 5 Qtz dissolution in a IA-IIA mixture yields significant clue to mechanism.

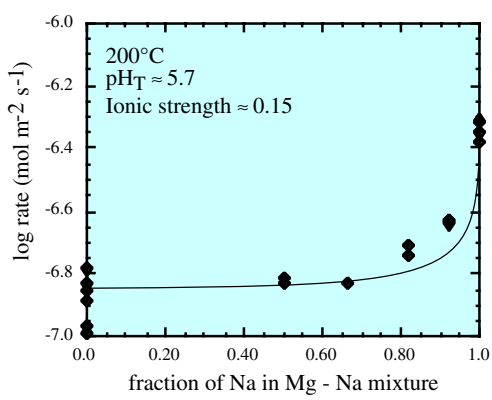
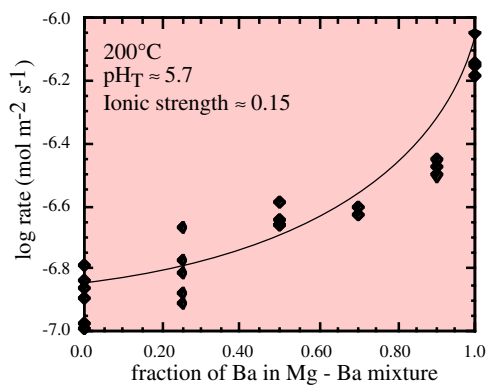


Fig. 6 Qtz dissolution in a IA-IIA mixture.



***Kinetics of quartz and amorphous silica dissolution in solute mixtures.* (Lorier, *M.S. Thesis*, Georgia Institute of Technology, Atlanta; Lorier and Dove, in prep., *Geochim. Cosmochim. Acta*).** Troy Lorier will successfully complete a M.S. thesis this spring semester (May 2000). As a step towards quantifying silica behavior in the complex solution compositions of natural systems, this study determines the influence of major solutes found in subsurface waters on the dissolution kinetics of quartz and amorphous silica. Dissolution rates were measured using mixed flow-through reactor (MFR) systems as a function of solute concentration for the individual cations sodium, potassium, calcium, and magnesium, at 200°C and pH 5.7. Each of the major solutes increases the dissolution rate of amorphous silica and quartz by 60 to 100 times, as compared to deionized water (no cations present), to an extent that is dependent upon the identity of the cation, i, and dissolved concentration. These were the first experiments of their kind and showed that the behavior of amorphous silica is similar to what we had observed for quartz (e.g. Fig 3). At the cation concentration range relevant to the composition of terrestrial waters, rate measurements show that calcium and magnesium have the greatest control on net rates **(Fig 7)**. The controls of mixed-cation solutions on dissolution rates are quantified by an empirical competitive surface interaction model. This model has a physical basis that is founded in the competitive interaction of each type of cation with the

silica surface. Magnesium and calcium have the greatest influence on net rates of dissolution because of their relatively large cation-surface interaction constants, compared to lower values for the weakly interacting sodium and potassium. These findings have allowed Troy to make an important step toward understanding silica reactivity in the more complex natural and waste-modified subsurface fluids by designing several simple solution compositions to simulate a small range of groundwater chemistries in higher temperature environments. **Fig 8** shows that the results of these first-of-kind experiments support the hypothesis that calcium and magnesium dominate net rates.

Counteracting solute effects- inhibiting dissolution by aluminum oxyhydroxides **(Dove, 1997, ISHR; Dove and Grantham, in adv. Prep.** ***Geochim. Cosmochim. Acta*****)**

In stepping towards the comprehensive model of silica reactivity, we are determining how higher valence ions inhibit dissolution rates and hence, counteract the rate-enhancing effects of major solutes. We have quantified the influence of aluminum (IIIB) on quartz and amorphous silica dissolution rates in parallel kinetic and microscopic studies. Sorbed aluminum is qualitatively known to affect

Fig. 7 Findings suggest that major solutes calcium and/or magnesium may control rates despite low concentrations in most environm.

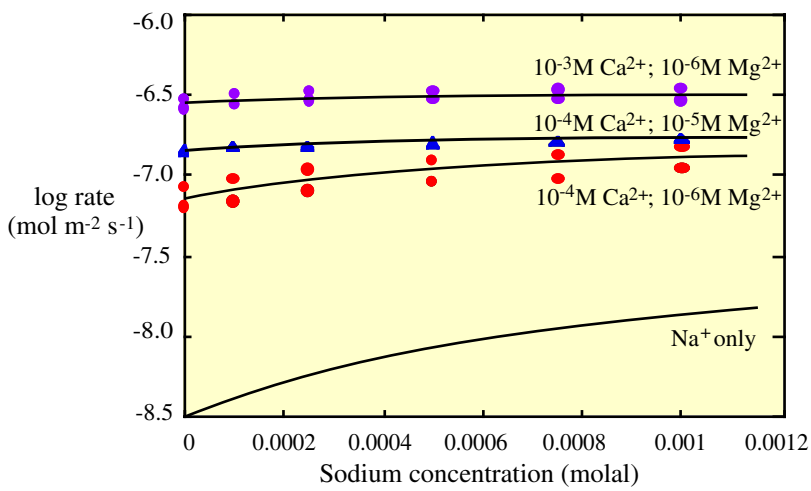
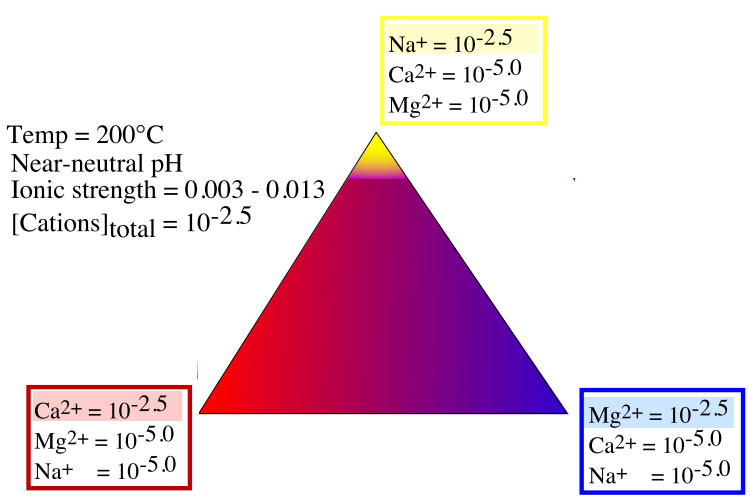


Fig. 8 Though sodium is most abundant solute, stronger interactions of Ca and Mg may control rates of silica dissolution.



Lorier and Dove (in prep.)

the surface properties, apparent solubility, and inhibit the dissolution kinetics of silica polymorphs (Iler, 1973). These studies (Hurd, 1973; Iler, 1973) are sometimes cited as evidence that aluminum inhibits the dissolution rate of silica by three to five orders of magnitude. However, our hydrothermal and low temperature studies (Dove et al., 1995; Dove and Grantham, in adv. prep; Icenhower and Dove, in adv. prep.) determined that quartz and amorphous silica dissolution rates are inhibited by a factor of less than 10 when solutions contain as much as 50 µmolar Al (as $AlCl_3$) (e.g. **Fig. 9**). These rate-inhibiting effects are observed across the 30 - 300°C temperature range: from low temperatures where gibbsite formation is stabilized to hydrothermal solutions (e.g. **Fig. 10**) supersaturated with respect to boehmite (e.g. Wesolowski, 1992). The energetics of dissolution are significantly modified in the presence of aluminum. Measurements of the temperature dependence show that experimental activation energies increase from 80±2 to 95±4 kJ mol^{-1} when 10 µmol Al is introduced to DIW or salt solutions.

Because our observations of the modest rate-inhibiting effect conflicted with widely accepted notions, we were initially skeptical of these findings. To ensure that these results were not due to an experimental artifact caused by minute surface abrasion of the Al(OH) precipitates, we conducted crosschecks using recirculating reactors designed to avoid all possibilities of surface disturbances. Rate data collected by this method (Dove and Grantham, in adv. prep.) confirmed the relatively small rate-inhibiting effect of aluminum.

Fig. 9. Aluminum inhibition of quartz dissolution kinetics at pH_T 5.7 is sensitive to NaCl concentration.

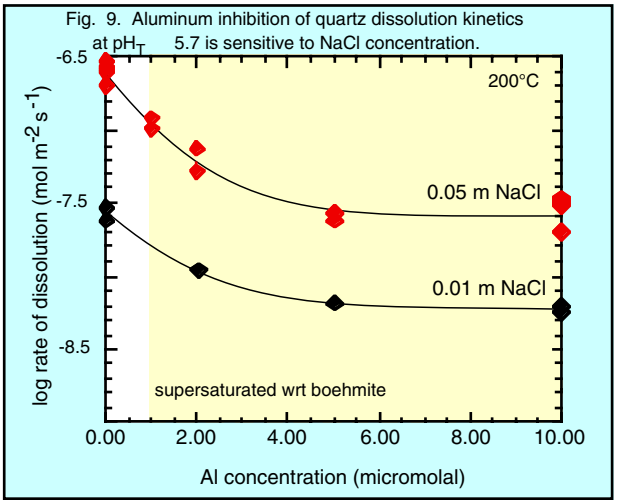
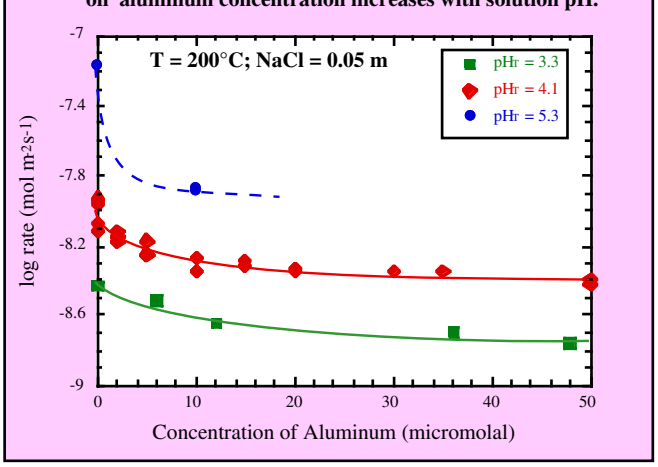


Fig. 10. The dependence of quartz dissolution kinetics on aluminum concentration increases with solution pH.



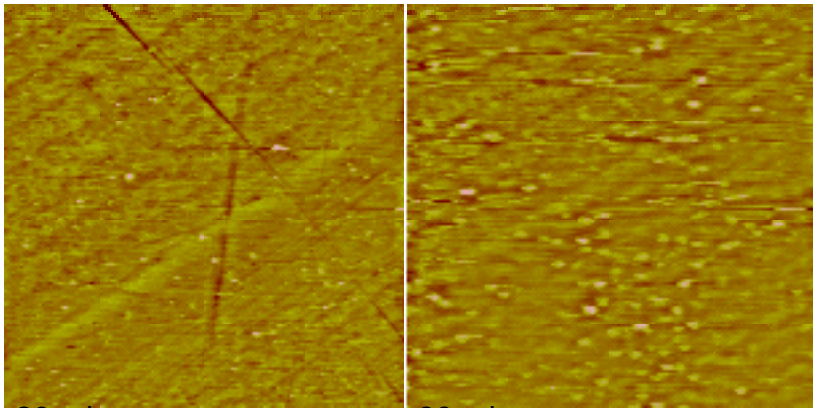
We also found that the extent of rate inhibition is dependent upon NaCl concentration as shown in **Fig. 10**. This cannot be explained by aqueous complexation (Dove and Grantham, in adv. prep.). This was another unexpected result because the aluminum-silica surface interaction strength is well known to be 10^4 to 10^9 greater than for sodium-silica (Iler, 1979). This suggests that sodium boosts *net* rate of silica dissolution independent of aluminum inhibition or sodium reduces the effectiveness of aluminum as an inhibitor.

Though the rate-inhibiting effect of aluminum is small, microscopic observations by in situ Atomic Force Microscopy document extensive accumulation of aluminum oxyhydroxide coatings on silica surfaces. The data are consistent with studies using other methods (e.g. Hem et al., 1973; Brown and Hem, 1975). **Fig. 11** illustrates the rapid accumulation of aluminum oxyhydroxide sorbates/precipitates in sequential *in situ* AFM images of a (110) quartz surface after 30 (left) and 90 minutes of exposure to 10 µmolar $AlCl_3$ solutions at pH 5.6. As surface begin to form with initial heights of 20-50 Å and diameters of 50-200 Å, the underlying silica surfaces becomes quickly physically isolated from contacting solutions. Surfaces exposed to aluminum-bearing solutions from low temperature experiments as well as surfaces from hydrothermal studies show that sorbates/precipitates soon become coatings with thicknesses on the order of 100's of nanometers. XRD and SEM analyses are unable to detect the presence or crystallinity of a coating on Al-treated quartz surfaces, but mas-NMR spectra of ^{27}Al indicate that the coating contains Al in VI coordination which is consistent with an amorphous and aluminum coordination chemistry at these conditions (Merino et al., 1989).

Our quantitative findings that aluminum has a relatively small rate-inhibiting effect have received considerable interest because of the ongoing controversy regarding probable mechanisms by which aluminum inhibits dissolution of amorphous silica. The 'silica problem' revolves around discussions of whether aluminum reduces H_4SiO_4 concentrations in natural waters by reducing silica solubility or by slowing rates of reaction (Lewin, 1961; Hurd, 1973; Wollast, 1974, 1983; Van Bennekom and van der Gaast, 1976; Van Bennekom, 1981; Van Bennekom, 1988; Van Bennekom et al., 1989; Van Bennekom et al., 1991). Explanations for the mechanism are still being evaluated. Our findings cannot yet entirely resolve the solubility question but clearly indicate that aluminum affects the kinetics of dissolution. Measurements of higher energies of activation indicate that Al-O-Si interactions lower the reactivity of silica surface structures. This is supported by theoretical studies (Lasaga and Gibbs, 1990; Xiao and Lasaga, 1996; Koretsky et al., 1998).

***Silica surface charge in IA and IIA electrolyte solution* (Craven, *M.S. Thesis*, Georgia Institute of Technology, Atlanta; Karlsson et al., submitted, *Geochem. Trans.*; Craven et al., in prep., *Geochim. Cosmochim. Acta*).** The mechanisms by which major solutes enhance rates of silica dissolution continue to be controversial (see later discussion). One hypothesis to explain this behavior proposes that the hydrated cations play an indirect role by forming outer-sphere complexes that affect the capacitance of the mineral-water interface (Karlsson et al, submitted). In this model, the protons and hydroxyls perform the dissolution mechanisms while the cations alter the state of surface

Fig. 11 In situ AFM images show 7 Angstrom steps on quartz (110 surface and precip nuclei w/exposure to 5 micromol Al.



protonation. To test this hypothesis and to develop a quantitative understanding of controls on silica surface charge development, new work by Karlsson et al. (submitted) and Craven (2000) are acquiring very high quality surface charge measurements. This new expertise promises to build an unprecedented quantitative understanding of charge development on silica surfaces. If the model is correct, silica surface charge and dissolution rates, with respect to solution electrolytes, should be dependent upon the hydrated radius, valence and concentration of the counterion at the interface. Preliminary potentiometric titration experiments have measured the dependence of silica surface charge development in a suite of metal chloride solutions (NaCl, KCl, $CaCl_2$, $SrCl_2$) (Fig 12). The data are showing that cation-specific changes in surface charge may partially account for variation in macroscopic dissolution (Fig 13). This correlation of aqua ion chemistry to the surface charge density of silica could possibly explain the rate-enhancing effects of cations by linking surface charge to rate equations of the form proposed by other authors for various silicate and oxide minerals (Wirth and Gieskes, 1979; Guy and Schott, 1989; Furrer and Stumm, 1986; Blum and Lasaga, 1988).

Fig. 12 SiO2 surface charge density in various electrolytes.

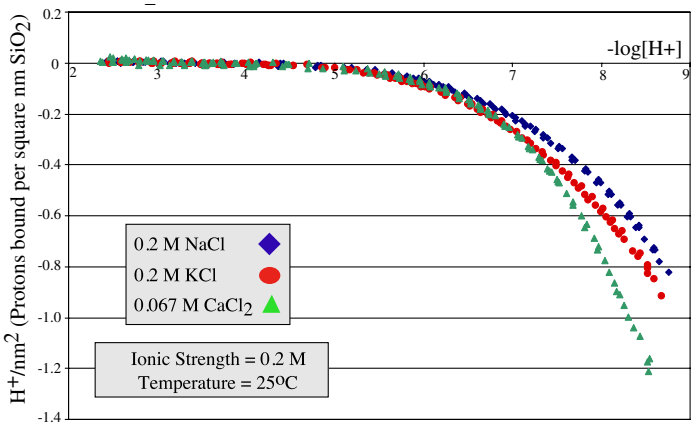
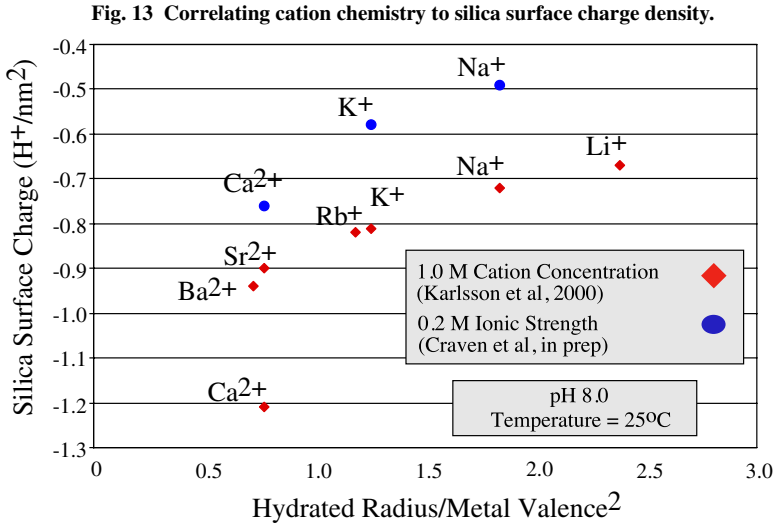


Fig. 13 Correlating cation chemistry to silica surface charge density.



Information Access

Published Manuscripts & Abstracts

Icenhower, J.P. and **P.M. Dove** (in press) The dissolution kinetics of amorphous silica into sodium chloride solutions: Effects of temperature and ionic strength. *Geochim. Cosmochim. Acta*.

Dove, P.M. (1999) The dissolution kinetics of quartz in dilute salt mixtures. *Geochimica Cosmochimica Acta*. **63**. 3715-3727.

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Publications Submitted or in Advanced Preparation

Craven, C.M., M. Karlsson, W.H. Casey, and **P.M. Dove** (in review) Surface charge of amorphous silica in electrolyte solutions and implications for dissolution. *Geochemical Transactions*. (new web-based ACS journal)

Dove, P.M. and M.C. Grantham (in advanced prep.) The dissolution kinetics of quartz in aluminum-bearing solutions in hydrothermal solutions. for *Geochimica et Cosmochimica Acta*.

Craven, C.M., M. Karlsson, W.H. Casey, and **P.M. Dove** (in advanced prep.) Silica surface charge in IA and IIA electrolyte solutions: Resolving the controls of ionic strength on charge development. For *Geochim. Cosmochim. Acta.*

Lorier, T. and **P.M. Dove** (in advanced prep.) Kinetics of quartz and amorphous silica dissolution: Effects of IA, IIA and aluminum in low temperature and hydrothermal solutions. for *Geochim. Cosmochim. Acta.*

Mixing Processes in High-Level Waste Tanks

Project ID: 54656

Dr. Per F. Peterson, University of California at Berkeley

Research Objective

Mixing and transport in large waste-tank volumes is controlled by the multidimensional equations describing mass, momentum and energy conservation, and by boundary conditions imposed at walls, structures, and fluid inlets and outlets. For large enclosures, careful scaling arguments show that mixing is generated by free buoyant jets arising from the injection of fluid or buoyancy into the enclosure, and by temperature and/or concentration gradients generated near surfaces by heat and mass transfer at walls, cooling tubes, and liquid-vapor interfaces. For large enclosures like waste-tank air spaces, scaling shows that these free and wall jets are generally turbulent and are generally relatively thin.

When one attempts to numerically solve the multi-dimensional mass, momentum, and energy equations with CFD codes, very fine grid resolution is required to resolve these thin jet structures, yet such fine grid resolution is difficult or impossible to provide due to computational expense. However, we have shown that the ambient fluid between jets tends to organize into either a homogeneously mixed condition or a vertically stratified condition that can be described by a one-dimensional temperature and concentration distribution. Furthermore, we can predict the transition between the well-mixed and stratified conditions. This allows us to describe mixing processes in large, complex enclosures using one-dimensional differential equations, with transport in free and wall jets modeled using standard integral techniques. With this goal in mind, we are constructing a simple, computationally efficient numerical tool which can be used predicting the transient evolution of fuel and oxygen concentrations in DOE high-level waste tanks following loss of ventilation, and validate the model against a series of experiments.

Research Progress and Implications

This report outlines research progress made since September, 1998, in our studies of mixing processes in high-level waste tanks, and requests permission for a one-year no-cost extension to complete the remaining tasks outlined in our original grant proposal, as a part of completing the dissertation of the primary doctoral student working on this research project.

Over the last year we have made substantial progress in our research efforts, both in experiments and numerical model development. In coordinating our spending rates and task completion, we recognized the importance of having our primary doctoral student working on the project, Jakob Christensen, completed his dissertation on the topic. Our request for a one-year no-cost extension will allow him to complete the writing of the dissertation, which will insure broader dissemination of the experimental and analytical results. A second doctoral student, funded by General Electric, is working concurrently studying mixing processes in large, stratified volumes, along with a postdoctoral researcher who has focused on the experimental program. Additionally, one Masters student has completed his research project supporting the study.

Our studies focus on the mixing processes that control the distribution of fuel and oxygen in the air space of DOE high-level waste tanks, and the potential to create flammable concentrations at isolated locations, achieving all of the milestones outlined in our proposal. A major motivation for the research has come from efforts at Savannah River to use a large tank process (Tank 48) for cesium precipitation from salt solutions, which release benzene. Under normal operating conditions the potential for deflagration or detonation from these gases would be precluded by purging and ventilation systems, which remove the flammable gases and maintain a well-mixed condition in the

tanks. Upon failure of the ventilation system, due to seismic or other events, however, it has proven more difficult to make strong arguments for well-mixed conditions, due to the potential for density-induced stratification which can potentially sequester fuel or oxidizer at concentrations significantly higher than average. As evidence of the importance of the issue, last year a decision was made to move away from the in-tank precipitation process. While this reduces the direct relevance of the research to SRP tank operations, important applications remain for modeling of radiolytic hydrogen mixing in large tanks, modeling of enclosure fires, and modeling of reactor containment response.

Our mixing experiments have two primary components: a series of experiments conducted in plexiglas tanks studying scaled mixing processes in water and water/salt or water/sugar systems, and a larger experiment in a scaled SRP-tank-geometry cylindrical enclosure using heated air to study mixing under stratified conditions, driven by combined natural and forced convection heat transfer. Substantial progress was made in conducting the water experiments during the past year, and completion of the large tank experiment was also achieved.

The water experiments completed this year have addressed two issues of importance to waste tank operations, as well as more generic problems in enclosure fires. The first involved the study of exchange flows through perforated horizontal partitions. Such exchange flows, driven by buoyancy and fluctuating external pressure, are the primary mechanism bringing ambient air into waste tanks through the many openings in the tank cover, following loss of ventilation. Our experiments, described in the the appendix of last year's report and in reference [1], provided fundamental information for modeling exchange flow rates into the tank vapor space.

These experiments also allowed us to simulate the evolution of the vertical density and composition distribution in a stratified volume. The primary question here is how a dense, buoyant plume of air would mix upon entering a tank from the ceiling, and how much dilution would occur before the plume reached the tank liquid, where fuel concentrations would be the highest. The water system provided a useful analog for this process. In addition to employing standard techniques to measure the velocity of the jets entering the bottom volume of the experiment (hot film anemometry) and to visualize the buoyant jets (ink), we developed a new experimental method to measure the vertical density distribution directly, using the deflection of a sheet laser to measure the vertical distribution of the index of refraction, as described in greater detail in the appendix.

Construction of the air experiment is complete, and data will be collected over this summer. As described in the proposal, this experiment will allow the study of mix processes under scaled conditions more closely matching waste tank conditions.

Planned Activities

During the upcoming year we will complete experimental data quisition for mixed convection heat transfer in a cylindrical enclosure with an injected purge jet. This work will be augmented by benchmarking studies with the detailed numerical model now under development. Upon completion, modeling results and insights will be transferred to support waste-tank safety basis calculations. In addition, the significantly more general treatment of the new model, compared to zone models, will provide improved analysis for building fire and reactor containment applications.

Information Access

Additional information about this research project can be found at:
http://www.nuc.berkeley.edu/thyd/peterson/tank.html

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Foaming in Radioactive Waste Treatment and Immobilization Processes

Project ID: 60143

Darsh T. Wasan, Illinois Institute of Technology

Research Objective

The Department of Energy's (DOE) Savannah River Site (SRS) is responsible for the safe storage, processing and immobilization of the High Level (radioactive) Waste (HLW) currently stored in approximately fifty million-gallon underground storage tanks. Foam is present in many areas of the HLW processing including HLW chemical processing, HLW evaporation and HLW cesium decontamination. Foam impacts the production rates of each of these facilities. The presence of foam during chemical processing and evaporation steps leads to slower production rates in the high level waste evaporators and in the Defense Waste Processing Facility (DWPF) waste pretreatment and may lead to higher capital costs or slower production in cesium decontamination. Also, excessive foam causes radioactive contamination of the condensate and equipment. Hence, the objective of this research is to study the mechanisms that produce foaming during nuclear waste treatment, to identify key parameters which aggravate foaming, and to identify effective ways to eliminate or mitigate foaming.

Research Progress and Implications

This report summarizes the work after two years of a three-year project. Laboratory tests were conducted at Illinois Institute of Technology (IIT) using a non-radioactive simulant slurry containing high levels of noble metals and mercury similar to HLW. The parameters which were found to play a key role during foam generation in this kind of three-phase system are the concentration of solids and particle size, heating temperature, electrolyte concentration, and organic and inorganic components. It was concluded that foaminess of the simulant sludge is due to the presence of colloidal particles and has a maximum when particle concentration is increased. The maximum in foaminess is attributed to the oscillatory nature of the potential of many-body particle interactions; because of structural stabilization of a foam lamella there is an increase in foaminess with concentration, but as the concentration further increases, because of the attractive depletion force (i.e. due to the excluded volume effect), there is destabilization of the foam lamella and thus reduction in foaminess. Based on this mechanistic understanding of foam generation and stability, an improved antifoam agent was developed at IIT, since commercial antifoam agents were ineffective. This improved antifoam agent was successfully tested in laboratory scale experiments at both IIT and SRS and in a pilot plant at SRS.

Planned Activities

Our recent experimental observations have also revealed that foaminess in the sludge simulant is due to the biphilic (exhibiting both hydrophilic-attracted to water- and hydrophobic-repels water) nature of the sludge solids. The biphilic nature of the solids leads to their accumulation at the liquid/air interface which results in stabilization of bubbles. We have designed a special experimental set-up using reflected light microscopy to monitor the attachment of the sludge particles to the gas-liquid surfaces. These measurements are fundamental to the understanding of factors which lead to an increase in foaminess. This research will lead to better future antifoam development.

Publications

This research work has been presented in the following conferences:

a. EMSP National Workshop, Chicago, July 27-30, 1998.
b. American Chemical Society Meeting, Dallas, March 29-April 2, 1998.
c. Industrial Advisory meeting of Interfacial and Colloid Phenomena Laboratory, IIT, Chicago October 22, 1999.
d. American Institute of Chemical Engineers meeting, Atlanta, March 5-9, 2000.
e. American Chemical Society meeting, San Francisco, March 25-29, 2000.
f. EMSP National Workshop, Atlanta, April 24-27, 2000.
g. One Master's Thesis entitled "Study of Three-Phase Foam Systems" by S.R. Bindal has been completed, IIT December, 1999.
h. Two papers based on this research have been prepared for publication.

Acoustic Probe for Solid-Gas-Liquid Suspensions

Project ID: 55179

Dr. Lawrence L. Tavlarides, Syracuse University

Margaret Greenwood, Pacific Northwest National Laboratory

Research Objective

The proposed research will develop an acoustic probe for monitoring particle size and volume fraction in slurries in the absence and presence of gas. The goals are to commission and verify the probe components and system operation, develop theory for the forward and inverse problems for acoustic wave propagation through a three phase medium, and experimentally verify the theoretical analysis. The acoustic probe will permit measurement of solid content in gas-solid-liquid waste slurries in tanks across the DOE complex.

Research Progress

As of June 30, 1999 we have completed two investigations concerning attenuation of sound in slurries. In Spelt et al. (1999a) we examined in detail the problem of predicting the attenuation of sound as a function of frequency for a suspension of spherical particles when the volume fraction of the particles is small. The theory, which accounted for the attenuation due to viscous, thermal, and scattering effects, was compared with the experiments for polystyrene particles in water and an excellent agreement was found. The same study also examined a more important problem of determining the size distribution of particles in a dilute slurry from the attenuation-frequency data for the slurry. A technique for solving this inverse problem was devised and the conditions under which it will be possible to determine the particle size distribution were determined.

In Spelt et al (1999b) we developed a theory for predicting the attenuation in nondilute slurries. This theory was tested against several known analytical results in various asymptotic limits and against experimental data on concentrated slurries obtained both in our laboratory and by previous investigators. The agreement between the theory and experiments, which covered wide range of particle sizes — from 0.1 micron to 200 microns, was very good.

We have also carried out attenuation measurements on gas-liquid and solid-gas-liquid systems. A theory was developed for predicting the attenuation for these systems. The experimental data showed the predicted trend that the noise due to bubbles must decrease as the frequency is increased when the frequency of sound waves is greater than the resonance frequency of the bubbles. Since the size distribution of the bubbles is not known a priori detailed comparison has not been made yet.

Planned Activities

It was shown in Spelt et al (1999b) that the data on phase speed of suspensions can be quite useful in determining the volume fraction of the particles. This is because the attenuation as a function of volume fraction of the particles can go through a maximum and the same attenuation can be obtained at two different volume fractions for a given frequency. The phase speed on the other hand changes monotonically with the volume fraction. Our present efforts are therefore directed at modifying the probe to also determine the phase speed of sound waves. In addition, we also plan to use a high speed imaging technique to determine the size distribution of the bubbles so that a more thorough comparison can be made between the attenuation data for the solid-gas-liquid systems and the theory. We also plan to develop a technique for the inverse problem for the three-phase slurries which would allow

one to determine the volume fraction of the solids even when the size distribution of the bubbles is not known

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Spelt P. D. M., Norato M. A., Sangani A. S., Greenwood M. A. and Tavlarides L. L. 1999b Attenuation of sound in concentrated suspensions: theory and experiments. J. Fluid Mech. (submitted).

On-Line Slurry Viscosity and Concentration Measurement as a Real-Time Waste Stream Characterization Tool

Project ID: 54890

Robert L. Powell, University of California

James Fort, Battelle Pacific Northwest National Laboratory

Research Objective

This work seeks to directly address the need for a robust technique to provide a comprehensive characterization of the rheological and other physical properties of tank slurries. In particular we have developed two techniques that have the potential to be used as an in-line viscometer to measure the viscosity of complex wastes during processing or, even in the tank. Such an instrument allows for the more precise control of the rheological properties and thereby allows for better control of the process itself. Ultimately it leads to the possibility of processing wastes at higher concentrations and reducing the need for diluting the wastes prior to pipeline transfer.

The principal objective of this work is to provide the theoretical and experimental foundations for a new in-line viscometer that can be used for radioactive waste slurries. A secondary objective is to understand how the suspension microstructure affects the rheological properties in order to make estimates of the properties based on the properties of the particles.

Research Progress and Implications

As of March 1, 2000, this report summarizes work after 3 1/2 years of a 4-year project. There have been accomplishments in three areas, two involving in-line rheometry and the third dealing with modeling of suspensions.

We have developed two techniques for use as an in-line rheometer: nuclear magnetic resonance imaging (NMRI) and ultrasonic Doppler velocimetry (UDV). A central feature of both techniques is that they provide pointwise measurements of viscosity in flow with a non-uniform shear. In such flows, for example, pipe flow, it is expected that the viscosity of a complex liquid (e.g., slurry or polymer) will vary with the local shearing conditions. Hence, if the viscosity can be spatially resolved, then the variation of viscosity with shear rate will be known. With the NMRI, we have demonstrated that very accurate measurements of the viscosity can be obtained using pipe flow. We have tested the technique with a range of fluids and have found excellent agreement when compared with conventional rheometrical techniques. Typically, from a single measurement, we can determine the viscosity as a function of shear rate over one and one half decades of shear rate to within 5% of data obtained by a cone and plate viscometer. We can also directly measure the yield stress and obtain agreement to within experimental error. Further, we have developed design criteria that could be used if this technique were implemented on, for example, a transfer pipeline.

We have shown that UDV can also provide spatially resolved viscosities. This technique is not as developed as NMRI so that the accuracy is not as good. However, UDV offers the opportunity for a very flexible and cheap instrument that can work in hostile environments. It is also likely that we will obtain better accuracy once the influence of flow and the test material on the measured signals are known. There have been discussions of using such a device at the Hanford Site.

The modeling studies have sought to understand the influence of particle size and size distribution on the rheological properties of slurries. We have developed three-dimensional simulations that permit colloidal and Brownian effects to be modeled. Further, our simulations allow us to use populations of spherical particles of arbitrary size, assuming that the Reynolds number is very small. To date, we have obtained predictions for the sedimentation velocity for a suspension and the viscosity of a suspension of having particles of two different sizes.

Planned Activities

During the remainder of the grant period, we expect additional progress in two areas. First, we are seeking to better understand the effect of small-scale velocity fluctuations induced by the particles in a slurry on the signals measured with both NMRI and UDV. If we can characterize these, it should help increase the resolution of both instruments. Secondly, the modeling studies will be continued to fully map the impact of colloidal and particle size distribution effects on the rheological properties.

Mechanics of Bubbles in Sludges and Slurries

Project ID: 60451

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G. Terrones, Pacific Northwest National Laboratory
M. M. Denn, UC Berkeley, Lawrence Berkeley National Laboratory
S. M. Muller, UC Berkeley, Lawrence Berkeley National Laboratory
W. R. Rossen, University of Texas at Austin

Research Objectives

Previous studies have established that the waste level of 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 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 yr of a 3-yr project.

Progress has been made in each of the areas of modeling bubble behavior in continuum materials (sludges) from both a solid mechanics viewpoint and separately from a fluid mechanics viewpoint, 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 and 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- and oil-based simulants, but each has limitations. The data shows “hysteresis,” where the level depends on the pressure history in addition to the current pressure, indicating that some stresses must be overcome before 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 the 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 as well. It was also found that the pressure cycles are not symmetric and 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 solid).

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 still 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 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) to 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 to the modeling results to reconcile the differences between the observed behavior and the different modeling approaches.

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Mechanics of Bubbles in Sludges and Slurries: Modeling Studies of Particulate Materials

Project ID: 60451A

William R. Rossen, University of Texas at Austin

Research Objectives

Bubbles form within the slurry in waste tanks of the Hanford nuclear reservation by radiation-induced destruction of organics in solution and subsequent diffusion of the products to bubble sites. If the fraction of gas in the slurry reduces slurry density below that of liquid above it, a "rollover event" occurs, in which potentially flammable quantities of gas are released into the vapor space at the top of the tank. It is therefore important to monitor the gas fraction in the slurry. One means of doing so is by tracking the response of liquid level in the tanks to changes in barometric pressure. Interpreting these data requires knowing the effective compressibility of bubbles in the slurry, which can be affected by capillary forces. In addition, it is desired to relate the mechanical properties of the slurry to the volume fractions of gas, solids and liquid in the slurry. This project examines the process of diffusive growth of bubbles within a porous medium and the volume response of this population to a change in barometric pressure. On a separate track, it examines the mechanical properties of dispersions of gas, solid and liquid, and the effect of capillary forces between bubbles and solids on the yield stress and compressibility of the slurry (modeled as a deformable periodic dispersion).

1) Model effective compressibility of bubbles dispersed in a rigid porous medium. Account for capillary forces on bubbles that restrain bubble response to ambient pressure changes, and therefore affect compressibility of bubbles. Account for diffusive growth process in context of strong capillary forces, that may bias distribution of bubble sizes in population and thereby affect effective compressibility.
2) Model yield stress and effective compressibility of a dispersion of gas, solids and liquid (assumed here to be deformable), focusing on capillary interactions between solid and bubbles, and effects of these interactions on mechanical properties.

Research Progress and Implications

With approximately 6 months remaining in this three-year project, we have determined the following:

Capillary forces affect the effective compressibility of individual bubbles in a rigid porous medium. Specifically, capillary forces reduce the volume response of most bubbles to a decrease in pressure, except for bubbles poised in a pore constriction, which may expand outwards into the next pore with a jump. Most of the volume response of a population of bubbles reflects the jumps of the fraction of this population poised at pore throats. There is a hysteresis in the volume response of bubbles, because bubbles that jump outwards upon a decrease in pressure do not in general jump back upon a subsequent equal increase in pressure.

Capillary forces also affect the initial distribution of bubbles in the pore space. As compressible bubbles grow by diffusion, capillary pressure rises as bubbles grow into pore throats. As a result, gas pressure and chemical potential rises, and the driving force for further diffusion to the bubble decreases. As a result, the distribution of bubbles is further distorted, favoring more bubbles poised just short of pore throats, ready to jump at a decrease in pressure.

The model fits the behavior of the Hanford tanks. Unfortunately, the fit to the data is not unique. Therefore, it is not possible to determine gas compressibility uniquely with our model without additional information on pore geometry.

A two-dimensional (2D) model for a regular array of solids, bubbles and liquid indicates that capillarity produces a yield stress in a bubbly slurry even in the absence of colloidal forces between the solids. The behavior is similar to that of two-dimensional foams without solids: as the material is sheared, bubbles are stretched, resisting the deformation, until a threshold displacement at which the bubbles and solids spontaneously rearrange themselves. The resistance to deformation gives rise to a yield stress for the material. As with foams with no solids, the wetter the slurry, the lower the yield stress, and for sufficiently wet slurries the yield stress disappears.

The compressibility of such a 2D slurry, in the absence of capillary effects, would be the product of gas compressibility and gas volume fraction. In extreme cases, with very fine solids and bubbles, the compressibility of the slurry is further reduced by capillary forces. There is a kink in the plot of compressibility as a function of volume fractions of solids and gas, which appears to be similar to a second-order phase transition.

Planned Activities

In the remainder of the project period, we plan to complete the modeling of bubble growth by diffusion and gas compressibility, further examine the fit to Hanford tank data, and write final reports and articles for publication on all these topics.

Information Access

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Numerical Modeling of Mixing of Chemically Reacting, Non-Newtonian Slurry for Tank Waste Retrieval

Project ID: 65371

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Research Objectives

Many highly radioactive wastes will be retrieved by installing mixer pumps that inject high-speed jets to stir up the sludge, saltcake, and supernatant liquid in the tank, blending them into a slurry. This slurry will then be pumped out of the tank into a waste treatment facility. Our objectives are to investigate interactions—chemical reactions, waste rheology, and slurry mixing—occurring during the retrieval operation and to provide a scientific basis for the waste retrieval decision-making process. Specific objectives are to

- Evaluate numerical modeling of chemically active, non-Newtonian tank waste mixing, coupled with chemical reactions and realistic rheology
- Conduct numerical modeling analysis of local and global mixing of non-Newtonian and Newtonian slurries
- Provide the bases to develop a scientifically justifiable, decision-making support tool for the tank waste retrieval operation.

Research Progress and Implications

This report summarizes work done in 1.5 years of 3-year project.

Yield strength of the waste. The chemically reactive, computational hydrodynamic code, TEMPEST, was modified to account for the yield strength of non-Newtonian tank waste sludge and saltcake that resist mobilization by mixer pump jets. The modified code was tested to model mobilization of sludge with and without yield strength. Test results showed that the 18-m/s slurry pump jets burrow into the sludge bank and erode only portions of the sludge where the shear and normal stresses acting on the sludge are greater than or equal to the sludge's yield strength. This modeling capability was used to assess pump jet mixing for Hanford Tank 401-AZ-102 and is now assisting in tank waste mixing test plans at Hanford. Once validated with the results of the Tank 401-AZ-101 mixer pump test, this added modeling capability could be used to determine how many pumps are needed to mobilize the tank waste, and, with a given number of pumps, how much and how fast tank waste will be mixed.

Examine 2-D reactive transport simulation of tank waste. During mixing, the waste can undergo aqueous and solid dissolution/precipitation reactions. This phenomenon is being examined under four two-dimensional pump jet mixing setups: Newtonian and non-Newtonian wastes with and without chemical reactions having $NaNO_3$(s) and $NaNO_2$(s) dissolution during mixing. As shown in Figure 1, the study indicated that in addition to Newtonian and non-Newtonian rheology differences,

dissolution of these solids changed the amount of the solids in the tank and the waste's physical properties and rheology, further affecting waste mixing.

Examine realistic 3-D reactive transport simulation of tank waste. The TEMPEST code is being applied to more complex and realistic 3-D pump jet mixing with reactions of $NaNO_3$(s), $Na_2CO_3 \bullet H_2O$(s), and Na_2SO_4(s) with aqueous species of Na^+ NO_3^-, $NaNO_3$(aq), OH^-, CO_3^{2-}, SO_4^{2-}, NO_2^-, $NaNO_2$(aq), H_2O, and $Al(OH)_4^-$. The results will be evaluated to examine interactions of chemical and hydrodynamic processes.

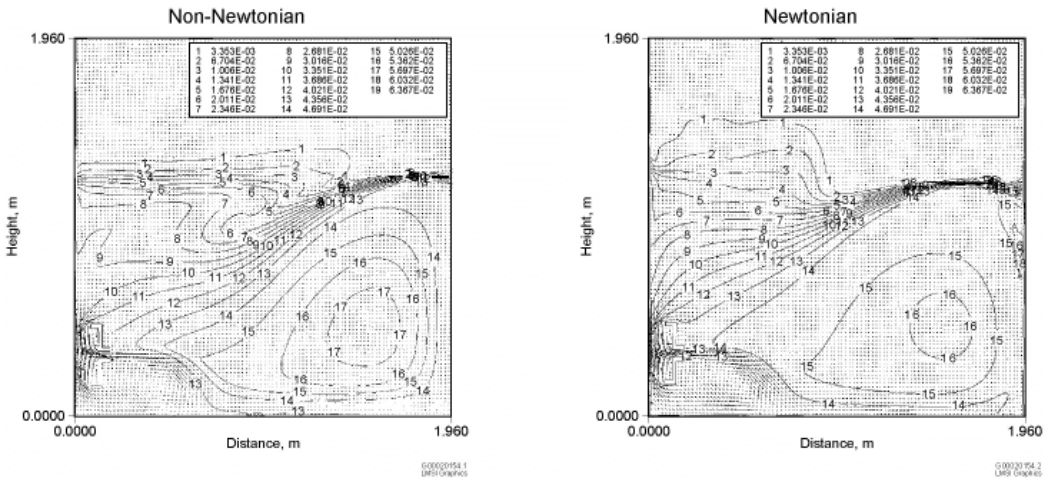

Figure 1. Predicted $NaNO_3$(s) distributions for 2-D Newtonian and non-Newtonian cases with chemical reactions at 20 simulation seconds

Numerical modeling analysis of local and global mixing of non-Newtonian and Newtonian slurries. It is important to evaluate local areas of unwanted chemical reactions not anticipated from small-scale laboratory experiments or coupled reactive slurry modeling by TEMPEST with coarse resolution. Thus, we will use the 2-D velocity field predicted by TEMPEST to conduct numerical modeling analysis of local and global mixing of non-Newtonian and Newtonian slurries. We will use a line method that is an extension of the particle method with the particles redistributed on the line dynamically with each time step. From mixing analysis, the Newtonian medium revealed a greater amount of stretching than the non-Newtonian material, which offers a natural scale-dependent resistance to deformation, preventing efficient mixing at smaller length scales (see **.edu/mixing/"** http://bobby.msi.umn.edu/mixing/).

Gibbsite and boehmite interactions and their mixing: During waste retrieval operations, if boehmite were to form instead of gibbsite, the slurry would become a gel and would be impossible to retrieve from the tank waste. We are developing a hypothesis for gibbsite and boehmite interactions and their associated rheology changes. This concept will be incorporated into TEMPEST to test its validity under 1-D test cases.

Planned Activities

We plan to continue to simulate coupled chemistry and mixing for tank waste for the 1-, 2- and 3-D test cases described above. Using the predicted velocity field obtained by TEMPEST, we will perform detailed local and global mixing for the 2-D cases. We will examine differences of mixing scales and degrees of Newtonian and non-Newtonian slurries and their implications on chemical reactions and slurry rheological changes. We will then compare these results with the coupled mixing and chemistry modeling results by TEMPEST, and we will use these findings to improve the scientific basis for developing retrieval operation decision-making support tools needed to determine the safety, design, and operational conditions of waste retrieval.

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http://bobby.msi.umn.edu/mixing/

Superconducting Open-Gradient Magnetic Separation for the Pretreatment of Radioactive or Mixed Waste Vitrification Feeds

Project ID: 55294

Richard D. Doctor, Argonne National Laboratory

Research Objective

Scientists need to gain a better understanding of the magnetic separation processes that can be used to separate deleterious constituents (crystalline, amorphous, and colloidal) in vitrification feed streams for borosilicate glass production without adding chemicals or generating secondary waste streams. This field work research describes how Argonne research staff and their partners will combine fundamental science with basic engineering to determine how magnetic separation can best be used for pretreatment of radioactive and mixed-waste vitrification feed streams. The results of this work will be used to reduce the volume and cost of high-level waste glass produced during U.S. Department of Energy (DOE) remediation activities. By elucidating the magnetic properties of constituents and their interactions with the chemical and physical environment, researchers will be better able to develop reliable models and efficient magnetic separation processes. Our proposed multidisciplinary technical approach involves using physical and chemical techniques to identify the magnetic constituents and radionuclides in the waste streams. The project will include the systematic study of magnetic interactions of waste constituents under controlled physical and chemical conditions (e.g., hydration, oxidation, temperature) to identify the mechanisms that control the magnetic properties. We will also study the partitioning of the radionuclides to determine their sorption mechanisms. The identification of fundamental magnetic properties within the microscopic chemical environment will be combined with development of hydrodynamic and electrodynamic models to understand the microscopic parameters for optimal magnetic separation. This project will lead to the effective use of superconducting open-gradient magnetic separation as a pretreatment technique for radioactive or mixed-waste vitrification feeds from DOE sites.

Electrically Driven Technologies for Radioactive Aerosol Abatement

Project ID: 65328

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Valmor F. de Almeida, Oak Ridge National Laboratory

Research Objective

The objective of this research program is to develop an improved understanding of how electrically driven processes, including electrocoalescence, acoustic agglomeration, and electric filtration, may be employed to efficiently treat problems caused by the formation of aerosols during DOE waste treatment operations. The production of aerosols during treatment and retrieval operations in radioactive waste tanks presents a significant problem of cost, worker exposure, potential for release, and increased waste volume. Electrically driven technologies offer promise as remote technologies for improved treatment; however, existing theoretical models are not suitable for performance prediction and design.

The basis for the project is the general fact that for most particulate collection technology, the marginal collection efficiency increases as the aerosol to be separated increases in size. Using this as a premise, we are investigating mechanisms for increasing the size of particles in an effluent stream as a preprocessing step. Our work is aimed at employing recent advances in theoretical approaches and experimental techniques to improve our understanding of how electrical and acoustic methods may be employed most efficiently alone or in tandem to tackle aerosol problems. The fundamental understanding achieved may provide the basis for development of innovative new approaches and for optimizing removal processes.

Research Progress and Implications

Following is a summary of the work after 9 months of a 3-year project. Progress in this project has been made both in identifying relevant DOE EM problems and in technical investigations.

Relevance to DOE problems: O. A. Ezekoye represented this project at the EMSP/TFA Workshop in Richland, Washington on November 17-18, 1998. This was a valuable meeting, describing in detail the problems associated with tank waste retrieval and treatment, and discussing the relevance of the EMSP projects to these problems. Washable ceramic and fritted metal filters have been identified as the primary treatment technology for aerosol loading in tank off-gas. Therefore, the DOE end-users have not placed electrically driven aerosol treatment as a high-priority item for tank waste treatment. However, through discussions with Mike Terry, Safety Technical Integration Manager for Tanks Focus Area, an alternative high-priority need was identified: aerosols produced from calcining operations (see ID-2.1.2). Experimental and theoretical investigations will be conducted for generic process situations with both waste streams in mind, focusing on the capability for removal of aerosols of size distribution, concentration, and density of those applications.

Technical progress: Through literature review and model testing of acoustic agglomeration dynamics of aerosol particles, we have ascertained that there is still an incomplete picture of particle-particle interactions in the presence of external fields. Design codes for agglomeration processes will require more accurate models. Unfortunately, the dynamics of acoustic and electric agglomeration

of the aerosols of interest occur on length scales that cannot be readily examined under realistic conditions. To address this problem, we have designed and built a simple experiment involving spherical particles falling through a vibrating glycerin bath. Experimental conditions have been designed to closely match those of acoustic agglomeration of aerosols. Experiments have begun, and the results are expected to provide needed information on relative motion of particle pairs.

Work has been performed to investigate the capabilities of an "acoustic barrier particulate separator" that is similar to a commercial technology under development. This separator employs secondary pressure fields to push small particles toward a collector. We are in the process of modifying an existing apparatus at UT-Austin to characterize the performance of the process and compare with existing theory.

Two additional experimental setups have been devised and are in the final design stage. The apparatus will allow fundamental, lab-scale research on the agglomeration of aerosols in flowing gas streams under controlled conditions with applied acoustic and/or electric fields. The experiments have been planned to take best advantage of the resources available to this project at UT-Austin and ORNL, and they will provide data on agglomeration and particle removal performance that can be directly compared with theoretical predictions. These experiments are expected to begin in July.

Planned Activities

We plan closely coupled experimental and theoretical work. Experiments will employ the apparatus described above to investigate particle-particle interactions at the fundamental level, and macroscopic particle agglomeration in flowing gas streams under applied fields. The experimental results will be compared with simulations for development and verification of design tools.

As stated above, current understanding of fundamental mechanisms responsible for acoustically enhanced agglomeration of aerosols is poor. Conventional models based in population dynamics rely strongly on unavailable information, at the particle-to-particle/fluid scale, embedded into collision frequency functions. We plan to advance the state-of-the-art of modeling in this area by fully accounting for interaction of particles and fluid. Exploiting terascale-computing power, we plan to apply lattice-Boltzmann methods to recover the Navier-Stokes regime of flow in fluid under the effect of an acoustic field while employing a Langevin equation to describe the motion of aerosol particles. On a second stage we plan to incorporate an electric field into the model to observe combined effects of acoustic and electric fields.

In parallel with our technical work, we will continue to develop contacts with end-users to determine relevance and feasibility for practical applications.

Information Access

No results have been published to date.

Detection and Characterization of Chemicals Present in Tank Waste

Project ID: 65340

Panos G. Datskos, Oak Ridge National Laboratory

Michael J. Sepaniak, University of Tennessee

Research Objective

The principal goal of this three-year project is to develop and demonstrate novel multi-parameter micro-electro-mechanical system (MEMS) sensors that are robust and can be used to simultaneously detect the presence of target chemicals in a mixture, radiation emitted from radioactive materials, and the heat generated by the absorption of photons of specific wavelength by the target chemicals. A major emphasis of this program is to study and develop effective methods of modifying MEMS surfaces with nano-scale structural features and chemical selective phases to improve sensor performance.

Research Progress and Implications

Research results after ~ 16 months of this 36 month project are described below.

Studies of Photo- and Adsorption-Induced Stress in Microstructures and Photothermal Spectroscopy

Micromechanical structures respond to chemical stimuli by undergoing changes in their bending and resonance frequency even when a small number of molecules adsorb on their surface. In our present studies, we extended this concept by studying changes in both the adsorption-induced stress and photo-induced stress as chemicals adsorb on the surfaces of *MCs*. By combining measurements of photo-induced and adsorption-induced stress in MEMS devices caused by target molecules with microcalorimetric spectroscopy both the presence and identity of target molecules can be determined. In addition, radioactive chemicals may also be identified by measuring the temperature changes of micromechanical sensors as they absorb emitted radiation.

(i) Studies of Adsorption-Induced Stress in MEMS. We investigated the effect of absorption of trace amounts of target molecules, 2-mercaptoethanol and diisopropyl methylphosphonate (DIMP), on micromechanical structures. Although gold coated surfaces adsorb DIMP effectively, the selectivity can be substantially improved by first coating the surface with self-assembled monolayers. The chemical selectivity of the layer is based on the interaction of Cu^{+2} bound to the MEMS surface by a carboxylate-terminated n-alkanethiol monolayer. Microcantilever MEMS devices with such surface coatings were exposed DIMP molecules by flowing a mixture of N_2 and DIMP vapor in a chamber containing the microcantilever. The modified MEMS respond proportionally and reversibly to the presence of DIMP molecules in a way that is distinguishable from any response to common organic solvents such as ethanol, methanol, or acetone.

(ii) Studies of Photo-Induced Stress in MEMS. In our studies, we used Au-coated Si microstructures to investigate the effect of molecular adsorption of DIMP and trinitrotoluene on the photo-induced bending of *MCs*. We measured the photo-induced stress before and after exposure to target molecules using a diode laser capable of delivering 10 mW and found that the photo-induced bending of microstructures depends on the amount of target analyte adsorbed on the surface of the MEMS device.

(iii) Studies of Photothermal Spectra Using MEMS devices. In the present studies we used our microcalorimetric spectroscopy technique and obtained photothermal IR spectra for trace quantities of target chemicals (e.g., 2-mercaptoethanol, toluene, anthracene).

Investigations of Chemically Selective Coatings to Enhance Sensor Performance

Several approaches are being pursued to influence sensor selectivity and sensitivity: *(i)* metal chelating resins are immobilized onto solid scintillator fibers,[1] *(ii)* polysiloxane (GC-type) phases are spin-coated onto microstructures,[2] *(iii)* mercapto-modified receptor phases (e.g., derivatized cyclodextrins, CDs) are chemical bonded to Au-coated microstructures. The underpinning aim of this effort is to selectively increase sensor response factors for environmentally significant analytes.

(i) Resins. Dual mechanism bifunctional polymer resin, that exhibits a high specificity for Cs in alkaline solutions, has been immobilized onto solid scintillation fibers. By optimizing conditions it has been possible to produce stable, field-ready fibers that retain resin and fiber functions. Based on a scintillation mode of operation for ^{137}Cs β-emission, these fibers were found to respond linearly over a range of 1.4 to 1120nCi, (3.4×10^{-10} to 2.7×10^{-7} M ^{137}Cs), with an LOD of ~0.025 ppb ^{137}Cs.

(ii) Polysiloxane phases. SP 2340 and OV 25 were spin coated onto Si microstructures at thickness ranging from 50 to 500 nm. The responses to vapor phase chemicals follow selectivity trends that are consistent with conventional methods of classifying these GC stationary phases. Film and microstructure thickness were shown to dramatically effect response sensitivity.

(iii) Cyclodextrins. CDs that are fully mercaptanated at the primary hydroxyl positions have been synthesized and characterized by NMR spectrometry. Procedures for bonding these receptors to various Au-coated surfaces are being explored. Surface plasmon resonance and actual *MC* measurements for these modified surfaces are being performed. Molecular mechanics modeling techniques are used to predict receptor-analyte binding characteristics and to guide the synthesis of new CDs. Results of employing this rational method of imparting selectivity to sensing using MEMS are preliminary at this stage.

Surface Modification to Enhance Sensor Performance

Preliminary studies have been conducted to modify the surfaces of microstructures to enhance response in a general sense and to increase the surface area for the immobilization of chemical selective phases. We have successfully spin-coated silicate, meso-porous, sol gels onto microstructure surfaces and begun to evaluate their response characteristic in native and chemically functionalized forms. In addition, single and multilayer Au nano-scale beads have been chemically attached to silica and smooth Au surfaces. We expect that these architectures will produce greater surface areas for the binding of receptor phases and produce greater lateral stress on microstructures (increase response sensitivity) upon inclusion of chemicals into the receptor cavities.

Planned Activities

Advances in surface modification will be combined with CD-based receptor phases to produce *MC* sensors with high sensitivity and selectivity. Photo-induced responses and photothermal spectra for target chemicals interacting with microstructures modified with nano-features and receptor phases will be obtained. The analytical figures of merit of this approach will be determined for a broadened set of target chemicals and synthetically generated receptor phases. We will continue to use molecular modeling techniques to aid in the rational design of chemically modified sensors. Eventually we will develop MEMS arrays with different receptor phases on the sensing elements. The interaction of MEMS devices with nuclear radiation (alpha and beta particles) will be studied to determine how the geometry and material properties of the microstructure affect such interactions.

Information Access

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Mass Spectrometric Fingerprinting of Tank Waste Using Tunable, Ultrafast Infrared Lasers

Project ID: 65425

Dr. Richard F. Haglund, Jr., Vanderbilt University

Dr. Wayne P. Hess, Pacific Northwest National Laboratory

Executive Summary

During the past year, we have initiated systematic studies of mass spectrometry of model tank-waste materials using both conventional nanosecond, single-frequency and tunable, subpicosecond mid-infrared lasers. In addition to making initial measurements, we have also constructed several new items of equipment for the experiment and begun to develop a model of the processes which lead to efficient desorption and ionization of organic molecules (*e.g.*, toluene, benzene, crown ethers) from sodium nitrate. Comparisons of nanosecond and picosecond lasers, and of infrared and ultraviolet lasers, have been especially instructive. These accomplishments are detailed in the following paragraphs.

Key experimental results. The main thrust of our effort is understanding the mechanisms of matrix-assisted laser desorption and ionization (MALDI) using $NaNO_3$ itself as the matrix. Most of the experiments involve using a tunable infrared free-electron laser to create ions by tuning into resonant vibrational bands of the matrix materials. The motivation for doing this is fundamentally to avoid having to dilute tank-waste materials with some other matrix material, thus generating a potential secondary waste stream. We have concentrated our experimental efforts on three particular aspects of the problem we set ourselves in the proposal:

- Demonstrating that we can detect desorbing organic molecular ions from $NaNO_3$ crystals and powders using tunable, infrared light from a free-electron laser;
- Comparative studies of ultraviolet and infrared MALDI, including studies in which exogenous matrix materials are added to the $NaNO_3$.
- Developing a physical model of the processes of desorption and ionization which can be used both to underpin quantitation and to give insight into the MALDI mechanism.

Our experiments and model-building in these three areas have confirmed the following results:

First, we can indeed detect molecular ions desorbed from $NaNO_3$ with high sensitivity, and there is a linear regime within which one could hope to obtain relatively accurate quantitation. While we are presently only in the low ppm range in terms of sensitivity, we are aware of a number of things we can and will do to enhance the sensitivity by several orders of magnitude. It may be of particular interest that we find the crown ethers, upon desorption, also can abstract and carry away an attached Na atom which shows up very clearly in the time-of-flight spectrum.

Second, particularly efficient ion production is obtained if one irradiates doped $NaNO_3$ at 248 nm after adding an appropriate ultraviolet MALDI matrix material (*e.g.*, dihydroxybenzoic acid). On the contrary, however, the addition of infrared MALDI matrices (*e.g.*, succinic acid or 4-hydroxy-α-cyano-cinnamic acid) to the $NaNO_3$ does not materially affect the ion yield, even though the added matrix materials have significant absorption at the 7.1 mm wavelength used to excite the NO_3 stretching vibration. We believe the difference between uv-MALDI and ir-MALDI in this respect may result from the comparatively greater efficiency for generating photoelectrons in the ultraviolet.

Third, the "phase explosion" model proposed by a number of researchers seems to describe our results quite nicely – but one should note that this is the first time there has been any experimental evidence for this in the infrared.

The fundamental picture of the phase explosion is this: If the optical absorption depth of the material is short compared to the characteristic thermal diffusion length, it is possible to create very high volumetric density of vibrational excitation at high intensity, because of the strong thermal confinement. Indeed, in experiments on $CaCO_3$, the isoelectronic cousin to $NaNO_3$, we have shown that the free-electron-laser pulses deposit two vibrational quanta in every CO_3 group in the optical absorption depth. Under these circumstances, the irradiated material reaches the critical temperature T_c for explosive vaporization before the deposited thermal energy has time to equilibrate, leading to the so-called "phase explosion." This should be especially productive of highly energetic ions and neutrals, and gives extremely efficient material removal from surfaces.

Development of laboratory apparatus. In our proposal, we stated our intent to construct a novel miniature time-of-flight mass spectrometer which would also be suitable for post-ionization studies of neutral atoms and molecules emitted during laser-induced desorption. This apparatus has now been constructed and will be commissioned in the laboratory during the summer of 1999. It is expected to provide much of the data needed to test our conjecture about the mechanism of desorption and ionization in the infrared, in particular, the "phase explosion" hypothesis described above.

Training of graduate students. During this past year, we have had two students who have participated actively in the MALDI studies: Michael Papantonakis and Michelle Baltz-Knorr. Mr. Papantonakis is approximately a year and a half away from completing his dissertation; he is spending the summer this year working with Drs. Michael Alexander and Wayne Hess in the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory. His focus is on problems of quantitation associated with tank waste and the potential for the use of compact ion-trap mass spectrometers with MALDI ion sources. Ms. Baltz-Knorr is just at the beginning of her dissertation program, but has become increasingly skilled in experiments and will continue actively working on the program during the coming year.

Publications and conference contributions A number of conference contributions and publications have been or will be prepared and presented as a result of this year's work. These include the following:

1. Plenary lecture, "The Future of Tunable, Ultrafast Lasers in Materials Analysis and Processing," R. F. Haglund, Jr., American Society for Mass Spectrometry, Dallas, TX, June 1999.
2. Invited talk, "The Role of Vibrational Excitation in Desorption and Ionization from Molecular Solids," Conference on Laser Ablation (COLA'99), Goettingen,Germany, July 1999.

Contributed papers will be presented in sessions dedicated to the scientific basis of nuclear waste analysis and management at the American Chemical Society meeting (New Orleans, August 1999), and Fall Meeting of the Materials Research Society (Boston, December 1999). Papers on MALDI studies of organic molecules on sodium nitrate have been or are in the process of being submitted to *Chemical Physics Letters*, *Thin Solid Films* and *Applied Surface Science*.

High Temperature Condensed Phase Mass Spectrometric Analysis

Project ID: 60424

Dr. James E. Delmore, Idaho National Engineering and Environmental Laboratory

Executive Summary

This program (in the 20th month as of this writing) was initiated with the goal of designing, constructing and operating a materials analysis instrument capable of obtaining a wide variety of chemical measurements on a material at high temperature. This instrument is being built around a quadrupole mass spectrometer. There are three main modes of obtaining spectra from the high temperature condensed phase material; surface ionization from the condensed phase, secondary ion mass spectrometry (SIMS, both static and dynamic modes) of the condensed phase, and electron impact ionization of vapor phase neutral species. The combination of the data from these three modes will allow the gleaning of chemical information concerning the nature of the chemical species present in both the condensed phase (solid or molten) and the vapor phase. The intended application is the identification of the chemical species present in materials at high temperatures. The logic behind performing these types of studies is that the chemical species present at high temperatures may be quite different from those present at lower temperatures, and may subsequently greatly alter the chemical reactivity and the volatilization of certain species. This has implication for the high temperature processing of various forms of waste.

The example that was presented in the proposal involved the identification of the chemical species of technetium(Tc), some of which are much more volatile at elevated temperatures than others. Specifically, Tc in the +7 oxidation state (the preferred oxidation state) can exist either as Tc_2O_7 or as TcO_4^-. The former is volatile at lower temperatures (mp=393K, bp=584K), and the volatilization of the latter is dependent upon the counter cation, but being an ionic material much higher temperatures are required. The factors that determine the equilibrium between these two species are rather poorly understood, and with the capability to readily measure relative concentrations of these different species it should be possible to gain new insights into this problem and others.

There are important waste management implications related to this chemical system. Tc is present in radioactive wastes that are treated by thermal processes. Because the form of Tc will determine how readily the Tc is released, understanding the chemical equilibrium and processes related to the conversion of TcO_4^-, in both the condensed and vapor phase, to Tc_2O_7 will provide important insights into the development of appropriate waste processing schemes. Rhenium chemistry closely matches that of Tc, particularly in regard to the oxide chemistry (which is the Tc chemistry of greatest importance for waste management), and hence will be used in place of Tc, at least for the initial studies.

Thus far, design and fabrication of the instrument has been the primary focus of the program. During the past year, development and fabrication of the ion optics has been the top priority. Extensive modeling with the ion optics program "SIMION" was performed on many different ion source designs. The preferred design was finalized only after extensive refining. The design was finalized this past April, and the conversion into engineering drawings was completed in May. This design carefully balances the competing demands of the three main operating modes, which is no simple task. A complete description of this source is beyond what can be included in this report, however, the salient features are as follows. The sample is contained in a small refractory metal tube that is resistance heated. The face of this source is at the focal point of the ion lens that transfers ions into the mass spectrometer. Thermal ions that give important information concerning the more readily

ionized species on the surface are transmitted directly from the surface of the source into the instrument. Two different ion guns, one for static SIMS and one for dynamic SIMS, are focused onto this surface. The static SIMS gun will be used to analyze the composition of the top layer. The dynamic SIMS gun will cause significant ablation of the surface and will be used for the analysis of material below the top surface. Since both the thermal and the secondary ions originate from the surface of the sample, the same focusing conditions are able to transmit ions into the mass spectrometer. The neutrals emitted from the surface of the sample are ionized by an electron beam focused from all sides to converge at a point just above the surface of the sample. Ions are produced from the neutral vapor species before they can diverge significantly. The ion optic models suggest that sensitivity for neutrals should be excellent, and it is thought that the analysis of sputtered neutrals should also be possible, although it is recognized that this is much more difficult. The ion optics are optimized to allow highly efficient transmission of ions from all these modes into the mass spectrometer. This source is now being constructed.

The vacuum system and other primary components of the instrument were designed and constructed concurrent with the design of the source. The vacuum lock and high temperature probe have been proven to operate reliably. An ultra high vacuum chamber with turbo, ion, gettering and LN2 pumping houses the instrument. The turbo pump is used to evacuate the main chamber from atmospheric pressure, and is also used to differentially pump the two ion guns and the vacuum lock. After initial evacuation with the turbo, the ion pump is used to maintain vacuum, with the LN2 and sublimator pumps being used to accommodate heavy loads during an analysis. The system pumps into the low 9's without bakeout. The quadrupole mass spectrometer is an Extrel with 0.75" rods and very high sensitivity. The data system is modeled after one developed in our laboratory, and operates the instrument in an efficient fashion.

In the remaining 16 months of this program the plan is to complete the instrument and to test it on a variety of samples. The testing plan has been scaled back to accommodate the level at which the program is funded. The main activity will be to synthesize a variety of materials and to test the factors that force the equilibrium between the various rhenium oxide species (as a surrogate for Tc). We have a variety of ideas to test, such as the extent to which complexation stabilizes the perrhenate anion. We suspect that this is the main factor driving the equilibrium, but this remains to be seen. The various rhenium oxide species are readily differentiated by these methods, as demonstrated by analyses we have performed on various individual instruments. By combining all of these functions (measurement of neutrals, thermal ions and surface analyses by SIMS) into a single instrument, these measurements can be made in rapid sequence on a single specimen, allowing superior interpretation of data.

Optically-Based Array Sensors for Selective In Situ Analysis of Tank Waste

Project ID: 60217

Gilbert M. Brown, Oak Ridge National Laboratory

Reza Dabestani, Oak Ridge National Laboratory
Peter V. Bonnesen, Oak Ridge National Laboratory
David R. Walt, Tufts University

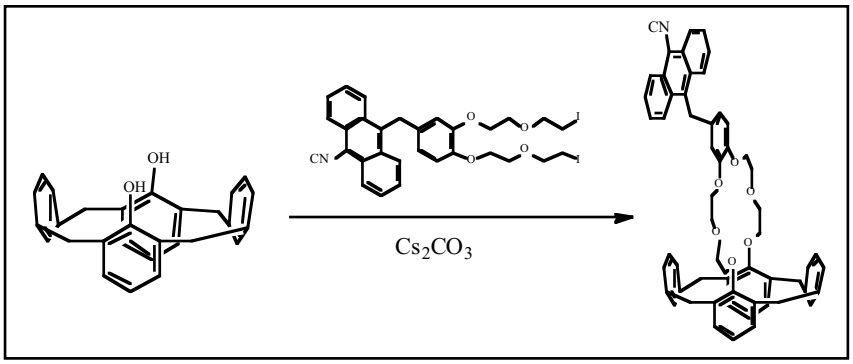
Research Objective

The objective of this research program is to conduct the fundamental research necessary to develop an array of chemically selective sensors, based on highly selective molecular recognition agents and highly sensitive fluorescence techniques, that can be coupled to fiber optics for remote analytical applications. These sensors will be of great value to DOE for the safe and cost-effective in situ characterization of high level waste tanks and other applications where remote sensing will prevent workers from being exposed to chemicals or radiation. The ability to detect and measure specific chemicals and radionuclides directly inside a high level waste tank using a remote sensing device could result in considerable benefits with regard to both cost savings and safety issues. In this approach to the design of sensors, agents for selective molecular recognition such as crown ethers are immobilized in an organic polymer matrix that mimics the organic medium in an aqueous nonaqueous extraction system.

Research Progress and Implications

Great progress has been made toward developing a fluorophore-selective ligand combination needed for a Cs^+ selective fluorescence sensor in the two years and 5 months of this project. Calix[4]bis-crown-6-ethers in the 1,3-alternate conformation have been shown to possess a high degree of selectivity for cesium over sodium and moderate selectivity for cesium over potassium. Several systems involving the preparation of a new class of calixarene-based ionophores having attached fluorescent probe molecules were demonstrated. Cyanoanthracene attached to the benzyl group of a benzo crown was prepared as the first generation of a cesium selective optical sensor. This fluorophore has been shown to be an effective fluorescence turn-on group, exhibiting a ten-fold increase in fluorescence when Cs^+ binds to the oxygens of the benzo crown moeity. The fluorescence of the 9-cyanoanthracene is quenched by the benzo moiety owing to a Photoinduced Electron Transfer (PET) process. It has been shown that binding of the oxygen electron pairs of the benzo moiety upon metal ion complexation partially suppresses the PET process, allowing the fluorescence of the cyanoanthracene to increase. The synthesis of a 1,3-alternate di-deoxygenated calix[4]arene-(9-cyano-10-anthrylmethyl)-benzocrown-6 **(1)** as the second generation cesium selective fluorescent probe has been accomplished by the route shown in the figure. This probe shows a 54 fold fluorescence enhancement response upon cesium complexation, which is the best result we have achieved to date. The selectivity ratios for this ligand to complex cesium over potassium and rubidium (K_{Cs}/K_K and K_{Cs}/K_{Rb}) are about ten fold higher than the first generation ligand. The observed selectivity ratios are consistent with data reported for other 1,3-alternate calix[4]dialkoxy-crown-6 derivatives. Work is in progress to translate these solution results to organic films.

In a new concept for utilization of these sensor elements, the application to the development of logic devices has been pursued. The high selectivity exhibited by calix[4]crown-6 ethers towards the complexation of alkali metal ions has been exploited to synthesize a supramolecular fluorescent



recognition agent capable of detecting both potassium and cesium ions in solution by PET. The new probe serves as a dual optical sensor to signal the presence of (a) potassium ions (as low as 10^{-6} M) in the presence of cesium ion (at concentrations as high as 5 x 10^{-4} M) under basic conditions and (b) cesium ions (10^{-7} M) without any interference from potassium ion at concentrations as high as 10^{-5} M in acidic media. The newly synthesized probe also behaves as an integrated logic gate combining an OR and a NAND gate for signal transduction. This is the first example of an integrated molecular logic device with feed back to the input of one logic element from the output of another.

Planned Activities

During the remainder of this fiscal year, we will focus our attention on the evaluation of the polymeric organic matrix that will be used to attach (and/or imbed) the ionophores to the fiber optic or to polymer beads including the necessity of adding modifiers. The objective is to maximize both selectivity and loading as a function of matrix variation.

Information Access

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Particle Generation by Laser Ablation in Support of Chemical Analysis of High Level Mixed Waste from Plutonium Production Operations

Project ID: 60075

J. Thomas Dickinson, Washington State University

Michael L. Alexander, Pacific Northwest National Laboratory

Research Objective

To provide fundamental mechanistic studies of laser-produced particulate formation in support of the analysis of radioactive and/or toxic materials by Laser Assisted–Inductively Coupled Plasma Mass Spectroscopy (LA/ICP-MS).

Research Progress and Implications

As of March 1, 2000 (six months remain in a three year project), we have characterized particle generation mechanisms laser ablation and their consequences in subsequent analysis by ICP-MS for model nitrates and waste glasses.

At typical laser power densities, analysis of both nitrate and waste glass materials show less scatter when UV laser wavelengths are employed. Work at PNL focused on waste glasses, because its more consistent response to laser irradiation facilitates comparisons among various treatments.

UV irradiation of waste glasses produces principally ultrafine aggregate particles which are readily digested in the plasma torch. However, EDX measurements on collected particles show significant deviations from the initial waste glass composition. These ultrafine particles are condensed from vaporized glass, where some glass components may preferentially vaporize and condense. High power density IR radiation produces many large fractured particles and large melted particles (> 2 μm in diameter) . These particles are not readily digested in the ICP-MS plasma torch, and may account for the relatively high scatter in LA/ICP-MS analysis when IR wavelengths are employed. However, EDX measurements of sample composition show that the composition of the fractured and large melted particles are quite similar to the waste glass composition.

The change in particle production mechanism as one moves from IR to UV wavelengths can be understood in terms of a thermal model of laser interaction. Both waste glass and the nitrates absorb much more strongly in the UV than in the IR. UV radiation heats a thinner layer of material to higher temperatures, allowing for efficient vaporization, followed by condensation into ultrafine particles. This process produces small particles that are readily digested in the ICP plasma, but also changes the particle composition.

Concurrent WSU focussed on the more intractable nitrates, using Cs- and Sr-doped single-crystal sodium nitrate as a model material. This effort examined the possibility of producing small fracture particles that can be analyzed reliably by ICP-MS. Three laser conditions were compared: high power density UV radiation (355 nm, particles principally condensed from vapor), high power density IR radiation (1064 nm, both melted and fractured particles), and low power density IR radiation (1064 nm, *principally fractured particles*).

High power density UV irradiation alters $NaNO_3$, quickly increasing UV absorption (incubation) and depleting volatile components (e.g., Cs). Although incubation and depletion are not desirable, the small particles produced by UV laser irradiation are more completely digested in the ICP-MS torch than the larger particles produced by IR. High power density IR irradiation depletes Cs relative to Sr; large fractured and large melted particles are produced. As expected, neither incubation nor

Cs-depletion are observed under low power density IR irradiation. Nevertheless, the particle size distribution was similar to that obtained at high IR power densities. However, the fracture particle size distribution evolves towards smaller particles as irradiation progresses.

Planned Activities

In the remaining six months of this project, we will continue to develop models for particle fracture and condensation to improve our fundamental understanding of particle generation and to provide guidance for optimization.

Studies will also be made of the ablation of conglomerate-type samples comparable to the saltcake found in the Hanford waste tanks. These samples are composed of particulates that range from less than one micron to hundreds of microns. Salt-cakes typically possess structure on a wide range of size scales, which should result in the generation of significant quantities of sub-micron particles by fracture. In addition, we will investigate large particle exclusion strategies (filters, cyclones, etc.)

Information Access

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Development of Advanced Electrochemical Emission Spectroscopy for Monitoring Corrosion in Simulated DOE Liquid Waste

Project ID: 60219

Digby D. Macdonald, Pennsylvania State University

Jun Liu, Pennsylvania State University
Sue Liu, Pennsylvania State University
Mohammed Al-Rifaie, Pennsylvania State University
Elzbieta Sikora, Pennsylvania State University

Research Objective

The principal goals of this project are to develop advanced electrochemical emission spectroscopic (EES) methods for monitoring the corrosion of carbon steel in simulated DOE liquid waste and to develop a better understanding of the mechanisms of the corrosion of metals (e.g. iron, nickel, and chromium) and alloys (carbon steel, low alloy steels, stainless steels) in these environments. During the first two years of this project, significant advances have been made in developing a better understanding of the corrosion of iron in aqueous solutions as a function of pH, on developing a better understanding of the growth of passive films on metal surfaces, and on developing EES techniques for corrosion monitoring. This report summarizes work on beginning the third year of the 3-year project.

Research Progress and Implications

A new rate law for the growth of a passive film on a metal surface has been derived. The new law, which is based on the Point Defect Model (PDM) for the growth and breakdown of passive films [1], is found to account for the transient in thickness of the anodic film on tungsten in phosphate buffer, under voltage cycling, much more accurately than does the High Field Model. We have used tungsten, rather than iron, for this analysis, because the passive film on W is a pure oxygen vacancy conductor (for which the theory for thickness transients is currently developed) and because experimental data are available from our previous work [2]. The theory is currently being applied to iron, but the required experimental data were not available at the time of preparation of this report.

The temporal change in thickness of the passive film on tungsten in phosphate buffer solution (pH = 1.5) as the potential is cycled from 10 V_{SCE} to 6 V_{SCE} and back to 10 V_{SCE} is shown in Figure 1 [2]. The experimental data were calculated from measured capacitance data and by assuming that the film could be modeled as a parallel plate capacitor with a dielectric constant of 35 [2]. However, the parallel plate model is not entirely appropriate, because a sharp drop occurs in the calculated "thickness" as the potential is stepped from 10 V_{SCE} in the negative direction. We previously [2] attributed this sudden decrease in apparent thickness to an artifact associated with a change in the space charge capacitance, an interpretation that was confirmed by also monitoring the change in thickness using optical reflectance measurements (no sudden change in thickness was detected using this latter technique). Excellent agreement is obtained between theory and experiment, which further supports the validity of the Point Defect Model. Finally, it is important to note that the High Field Model, which has been used for more than seventy years to describe the growth of anodic oxide films on metals, is unable to account for any of the data shown in Figure 1.

Although the passive state of iron has been extensively studied in the past, considerable disagreement exists as to the nature and composition of the passive film that forms on the metal

surface. This previous work has shown that the passive film formed on iron in borate buffer solutions has a bilayer structure comprising a defective inner Fe_3O_4 layer (the "barrier" layer, which grows directly into the metal) and an outer γ-Fe_2O_3 layer that forms by precipitation. The outer layer effectively screens the barrier layer from optical interrogation and also significantly modifies the electrochemical response of the surface. However, general agreement exists that the passivity of iron is primarily due to the barrier layer. Accordingly, the present work is based on the hypothesis that EDTA (ethylene diamine tetra acetic acid), which chelates the iron cations that are ejected from the barrier layer, should be effective in preventing the formation of the outer layer. If so, then the barrier layer alone may be investigated to provide a much more accurate account of the passive state. Our current work clearly shows that EDTA in borate buffer solutions effectively prevents the formation of the outer layer. Finally, passivation is enhanced by higher pH values of the solution.

The PDM (Point Defect Model), not the HFM (High Field Model), gives a better account of the kinetics of film growth. Furthermore, steady state polarization data show that the passive film on iron is an n-type semiconductor, due to a preponderance of oxygen vacancies and/or iron interstitials. Mott-Schottky analysis further confirms that the passive film formed on iron is an n-type semiconductor. The donor density of the barrier layer decreases and the steady state thickness increases linearly with increasing film formation potential, in agreement with the prediction of the PDM. Recent in situ X-ray diffraction studies by Toney, et. al. [3] also concluded that the passive film on iron is a "highly defective spinel oxide with a high concentration of vacancies and interstitials". However, these workers did not specify the exact nature of the defects. From the present work, we conclude that the dominant defects must be oxygen vacancies, which are generated by growth of the barrier layer into the metal, and Fe (II) interstitials, because of the n-type electronic character of the film. Cation vacancies cannot contribute substantially to the electronic structure, because they should impart p-type character.

A high fidelity method for measuring electrochemical emission data on carbon steel (AISI 1018: C 0.16, Mn 0.79, S 0.018, P 0.006, Fe balance) in alkaline solutions has been developed as a means of monitoring general corrosion and pitting corrosion of carbon steel in simulated DOE waste storage systems and to develop a better understanding of the mechanisms of corrosion of metals (iron) and alloys (carbon steel) in these environments. The initial goal was to demonstrate that noise data can

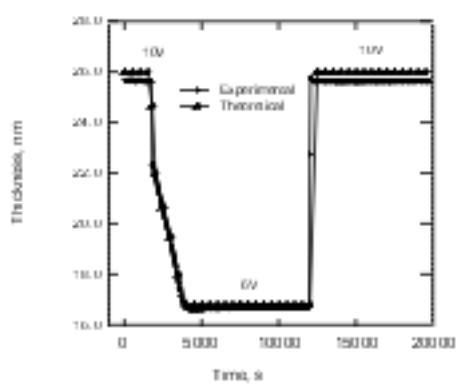

Figure 1. Transients in the thickness of the passive film on tungsten in phosphate buffer solution as the voltage is stepped from 10 V_{SCE} to 6 V_{SCE} and back to 10 V_{SCE}. The experimental values were measured using high frequency (1 kHz) capacitance. The theoretical values were calculated using Equation (4) and the parameter values given in Ref. 3. Note that allowance has been made for the sudden drop in thickness upon stepping the voltage from 10 VSCE to 6 VSCE, which is an artifact due to charging of the space charge capacitance. pH = 1.5.

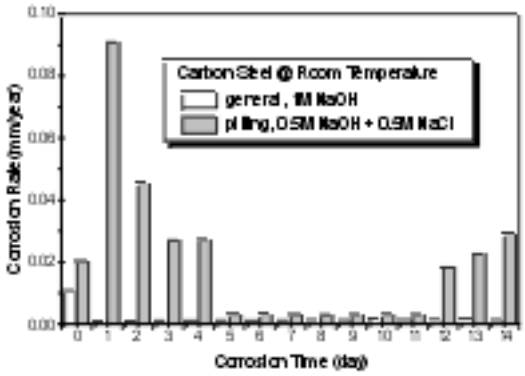

Figure 2. Comparison of penetration corrosion rates for general corrosion and pitting corrosion of carbon steel at room temperature.

yield corrosion rates that are of engineering relevance and can be used for estimating the integrated damage (loss of wall thickness). EES measurements are performed at the corrosion potential, making this monitoring technique more relevant to the actual conditions than is linear polarization, for example. The time domain data were transformed through Fast Fourier Transformation into the frequency domain, and power spectral densities (PSDs) were then calculated. An important quantity, the "noise resistance" (R_n), defined as the ratio of the standard deviations of the current and voltage fluctuations over a given time [4,5], was employed to derive the corrosion current densities and penetration corrosion rates shown in Figure 2. These data are in reasonable accord with data in the literature for similar systems.

In agreement with the recent findings of Edgemon, Danielson, and Bell [6], general corrosion on carbon steel in simulated waste systems is characterized by random fluctuations in current and potential. In passive systems, the fluctuations tend to decrease in frequency and magnitude with time as the passive film forms on the metal surface. In general, lower corrosion rates were associated with lower mean currents and smaller fluctuations in the current. Also, as shown by Legat [7], the correlation dimension and the maximum Lyapunov exponent of the electrochemical noise shows that localized corrosion is generated by a deterministic chaotic process, whereas uniform corrosion is a random (stochastic) process. Our study demonstrates that Electrochemical Emission Spectroscopy (EES) is a feasible, *in situ* technique for monitoring the corrosion of carbon steel in highly alkaline solutions of the type that exist in liquid waste facilities. Our future research will focus on general and pitting corrosion in different solutions and at higher temperatures. We will try to establish the link between the deterministic model (Point Defect Model, PDM [8]) and the "noise" due to metastable pitting.

We have now initiated the crack propagation studies that were scheduled for the final year of this program. The composition of DOE waste consists mainly of sodium salts with a high pH(>12). Accordingly, failure of the carbon steel storage tank by caustic cracking must be considered as one of principal threats to tank integrity. The emphasis in this part of our work is on exploring fundamental aspect of the caustic cracking mechanisms by using electrochemical emission spectroscopy (EES) to ascertain the dimension of the brittle micro fracture events that occur during crack propagation. Methods are currently being developed to measure the electrochemical emissions from growing cracks in the high strength, low alloy steel that was chosen to represent heat affected zones adjacent to welds in DOE storage tanks. A computer-based data acquisition system with a fast, multi-channel A/D board and a large buffer is being used to record the current and potential vs. time at a sampling frequency of 4 Hz. The loading and crack propagation measuring systems have been developed and are currently being assessed for accuracy. All specimens have been prepared and the first experiment is scheduled to begin during the week of February 28, 2000. These experiments are designed to provide fundamental information on the mechanisms of crack propagation.

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Planned Activities

Work will continue over the third year on all aspects of the program outlined above, with emphasis on EES and in particular on the ability of this method to monitor general corrosion rates and to discern the mechanism of stress corrosion cracking. Our theoretical work on passivity and on predicting localized corrosion damage will also continue, because it provides the basis for interpreting the experimental data and for estimating tank service life.

Publications and Presentations

Papers in press or in print:

1. D. D. Macdonald, "Passivity-the Key to Our Metals-Based Civilization", Pure Appl. Chem., 71(6), 951-978 (1999).
2. G. R. Engelhardt and D. D. Macdonald, "Modeling of Corrosion Fatigue Chemistry in Sensitized Stainless Steel in Boiling Water Reactor Environments", CORROSION/2000, Orlando, FL, March, 2000, Paper No. 00227 (NACE International, Houston, TX).
3. Sikora, E**.** and D. D. Macdonald, "Electrochemical and Photoelectrochemical Study of Passive Films on Iron Formed in the Presence of EDTA", Proc. Int. Symp. Hon. Prof. Norio Sato: Passivity and Localized Corrosion, Electrochemical Society, Princeton, N.J., in press (1999).
4. Macdonald, D. D**.** and D. F. Heaney, "Sequence of Events in the Breakdown of Passivity on Stainless Steels", Proc. Int. Symp. Hon. Prof. Norio Sato: Passivity and Localized Corrosion, Electrochemical Society, Princeton, N.J., in press (1999).
5. Sikora, J**.**, E. Sikora, and D. D. Macdonald, "Nature of the Passive Film on Tungsten", Proc. Int. Symp. Hon. Prof. Norio Sato: Passivity and Localized Corrosion, Electrochemical Society, Princeton, N.J., in press (1999).

Papers in preparation:

1. M. Al Rafie and D. D. Macdonald, "On the Transients in the Thickness of Anodic Passive Films on Metals", J. Electrochem. Soc., in preparation (2000).
2. E. Sikora and D. D. Macdonald, "The Passivity of Iron in the Presence of EDTA. I. General Electrochemical Behavior", Corros. Sci., in preparation (2000).
3. Jun Liu and D. D. Macdonald, "The Passivity of Iron in the Presence of EDTA. II. The Defect and Electronic Structures of the Barrier Layer", Corros. Sci., in preparation (2000).
4. S. Liu and D. D. Macdonald, " A Review of Caustic Cracking of Carbon Steel", Corrosion, in preparation (2000).

Conference Presentations:

1. Sikora, E**.** and D. D. Macdonald, "Electrochemical and Photoelectrochemical Study of Passive Films on Iron Formed in the Presence of EDTA", Proc. Electrochem. Soc. 197th Meeting, **99-2**, Abstr. 484 (1999).
2. Sikora, J**.**, E. Sikora, and D. D. Macdonald, "Nature of the Passive Film on Tungsten", Proc. Electrochem. Soc. 197th Meeting, **99-2**, Abstr. 490 (1999).
3. D. D. Macdonald and M. Al-Rifaie, "New Rate Law for the Anodic Growth of Passive Films", Proc. Electrochem. Soc. 198th May 14-19, 2000, Toronto, Canada.
4. J. Liu and D. D. Macdonald, "The Passivity of Iron in EDTA-Containing Solutions", Proc. Electrochem. Soc. 198th Meeting, May 14-19, 2000, Toronto, Canada.
5. D. D. Macdonald, "Mechanistic Analysis by Electrochemical Impedance Spectroscopy", Proc. Electrochem. Soc. 198th Meeting, May 14-19, 2000, Toronto, Canada.
6. D. D. Macdonald, "Fundamental Aspects of Passivity Breakdown", Corrosion & Prevention 2000, Nov. 19-22, Auckland, New Zealand.
7. D. D. Macdonald, M. Al-Rifaie, and G. R. Engelhardt, "Transient Growth and Reduction of Anodic Oxide Films on Metal Surfaces", Corrosion & Prevention 2000, Nov. 19-22, Auckland, New Zealand.
8. D. D. Macdonald, "Mechanistic Analysis by Electrochemical Impedance Spectroscopy", Corrosion & Prevention 2000, Nov. 19-22, Auckland, New Zealand.
9. D. D. Macdonald and G. R. Engelhardt, "The Deterministic Prediction of Localized Corrosion Damage", Corrosion & Prevention 2000, Nov. 19-22, Auckland, New Zealand.

Degrees Granted

The following degrees were granted to students who worked on this project over the past year:

1. Mohammed Al-Rifaie, Ph.D., "Identification of Point Defects Within Passive Films", May 1999. Present address: Assistant Professor, Department of Mechanical Engineering, University of Kuwait, Kuwait. Dr. Al-Rifaie was partially supported (stipend and academic fees) by the University of Kuwait.
2. Jun Liu, M.S., "Electrochemical Studies on the Passive Film on Iron", March 2000. Mr. Liu is continuing on this program for his Ph.D. degree.

Correlation of Chemisorption and Electronic Effects for Metal/Oxide Interfaces: Transducing Principles for Temperature-Programmed Gas Microsensors

Project ID: 65421

Dr. Steve Semancik, National Institute of Standards and Technology

Dr. Richard E. Cavicchi, National Institute of Standards and Technology
Dr. Thomas J. McAvoy, University of Maryland

Research Objective

This research project seeks to produce, and demonstrate the utility of, a scientific database for oxide conductometric sensing materials that relates materials performance (sensitivity, selectivity and stability) to composition, microstructure and temperature. This information and the capabilities derived from it would be applied to developing a robust, low cost and application-tunable chemical monitoring technology based on micromachined platforms.

Research Progress and Implications

The Report summarizes progress through the end of February, 2000, representing efforts for the first 17 months of a 3-year program. This program is creating the scientific and technical basis for gas and vapor sensors that work on a conductometric principle (adsorbed gases produce a change in electrical conductance) using low power, micromachined device platforms. In order to develop oxide-based microsensor arrays that can be tuned by choice of sensing film and temperature programming, we have worked in four parallel project areas: 1) development of advanced MEMs structures and arrays (platforms) with appropriate chemical and diagnostic functionality, 2) study of the process/property/performance relationships for semiconducting oxide films and metal/oxide interfaces, 3) mechanistic studies that examine temperature-dependent detection phenomena by relating changes in sensing film conductance with transient adsorbate coverages, and 4) combining mechanistic information and response databases with signal processing methods. More generally, this project has important implications relating to the use of microarrays and combinatorial methods in materials research, and in the examination of fast transient techniques to relate surface chemical and surface electronic phenomena.

Platforms *Micromachined structures are a critical part of this program. They are used both as platforms for fabricating solid state gas microsensors, and as research tools in efficient studies of materials*. Our original sensing device structure consisted of four individually-addressable and thermally isolated "microhotplates" (100 micron x 100 micron), which could be temperature controlled between 20°C and 500°C (8°C/mW and 3ms time constant). New platforms with flat surface topology (produced by chemical mechanical polishing) have been designed, fabricated and micromachined for this project. Arrays with 16, 36 and 48 elements are being employed as research tools for performing larger "growth/performance" studies, and for characterizing surface interactions. These new platforms include a 16-element array with on-chip control electronics, consisting of multiplexing, sample-and-hold, and amplification circuits, for running the microhotplates. An external data acquisition system used for controlling 36-element arrays, and for handling output signals has also been developed. The use of more elements enables a more efficient means of examining sensing materials combinations, film processing, and reproducibility. The increased number of elements also allows the incorporation of multiple sensing materials, varied modes of operation (fixed temperature and temperature-programmed), and system redundancy for reliability.

To learn more about the surface properties and interactions related to gas sensing, we are developing platforms tailored for the requirements of surface analytical tools. One such platform is a 340-element array for adsorbate coverage and desorption studies (see below). The large sample area is needed to generate enough desorbing molecules for mass spectrometer detection, while the small size of each element preserves the fast speed needed for rapid temperature pulsing. This structure will provide the first data that correlate transient electrical conductance measurements (measured with a number of on-array electrical contacts) in a sensor with thermally desorbed species. Another new device, a 600 micron, flat, single microhotplate element, is being developed to provide the large, uniform surface needed for spectroscopic techniques such as x-ray photoemission spectroscopy and Auger spectroscopy. We expect these tools to yield chemical state and composition data on sensing films both after fabrication and after exposure to analyte gases.

Array Studies of Materials Processing and Performance *Sensing material types and microstructures must be optimized for particular monitoring applications. Microhotplate arrays provide a very efficient platform for temperature-dependent film deposition and temperature-dependent response measurements.* During the first year of this project, studies of oxide film growth/performance were done using 4-element arrays. In recent months we have amplified the efficiency of our studies on microstructure controlled oxides by moving to 36-element arrays. A variety of methods for depositing SnO_2, each of which leads to its own characteristic type of microstructure, has been examined. These methods included self-lithographic CVD (using thermal activation to achieve selected-area deposition on microhotplates), reactive sputter deposition, drying sol-gels and nanoparticle suspensions (see also reference 1). Films fabricated by seeding the SnO_2 CVD growth with small metal particles (Ni, Co, Fe, Cu, Ag) have also been studied with 36-element arrays. Film reproducibility, as judged by SEM and sensing response, was investigated by making whole columns of films by the same recipe. Films prepared with seed layers and nanoparticle suspensions have shown reduced grain size, leading to enhanced gas sensitivity (for a number of gases in air). A second CVD system has been commissioned in order to do parallel deposition research on a number of other semiconducting oxide materials.

We have also begun screening the performance of various surface-dispersed catalytic additives (on seeded SnO_2 films) using 36-element arrays. The catalysts are being deposited by evaporation to varied (1-7 nm) thicknesses, and then the microhotplates are heated to affect the formation of a noncontinuous layer of catalyst particles on the SnO_2 surfaces. As for the oxide response evaluations, these samples will be studied in a collection of gases (including dilute concentrations of acetone, ethanol, benzene, methanol, and toluene, in air) to develop temperature-dependent sensitivity data. Improvements to sensor testing hardware have been made in order to increase data handling to the level required for larger numbers of samples in the larger arrays.

Mechanistic Studies *Temperature-dependence of adsorption/desorption, reaction, and other phenomena are the basis on which temperature-programmed sensing is built.* A specially-outfitted vacuum system is required for the desorption studies which will correlate surface electrical changes to adsorbate coverages for sensing films. Two types of experiments will be done: one involving a static-mode gas dosing followed by pulsed desorption from a 340-element microarray, and one that will explore dynamic features with microelement temperature pulsing, beam dosing to examine elevated pressure regimes, and differential pumping. Construction of this system is now complete. The vacuum chamber, mass spectrometer and multiple pumps have been put through initial tests involving desorption from macrosamples (~ 1 cm^2). High resolution and rapid thermal imaging has been used to examine the temperature uniformity of the microhotplate array elements. Sample preparation on 48-element and new 340-element arrays are now underway.

Since rapid thermal modulation is used in the temperature programmed operation of the microhotplate sensors, experimental measurements were made (in collaboration with the University of Maryland) to determine the role that trap states might play in the measured electrical responses following purposeful thermal transients. To establish a non-chemical (no analyte) environment, measurements were made in an argon background, and an air background. Modeling of these data with shallow trap states provides good agreement with the measurements.

Signal Processing *Signal processing studies of the rich data content from temperature-programmed*

individual microsensors and array elements are critical for proper analyte recognition and quantification. The major modeling effort (a collaborative activity with the University of Maryland) is scheduled for the latter two-thirds of this project, when multi-element, temperature dependent databases are available. As a precursor to that work, we have initiated preliminary testing of sensitivity and stability as they relate to neural net training and predictive model development. Preliminary findings on several types of films show trade-offs between sensitivity, stability and selectivity. We have also used techniques based on earlier work with temperature programmed sensing to recognize a single analyte in air and estimate its concentration (reference 5).

Planned Activities

In the remainder of FY00, efforts will focus on:

- Platforms - development of improved metallization for the microdevices and research arrays
- Materials Studies – measurements on 36-element arrays producing temperature-dependent databases of sensitivity for metal/oxide film combinations for a spectrum of analytes in air; critical studies to establish stable microdevice operation and acceptable sensitivity and selectivity (required for signal processing work)
- Mechanistic Studies – initial measurements from 340-element arrays directly correlating conductance changes with desorbed species
- Signal Processing – selection of stable films for training experiments and development of models for single analytes (in air) within acceptable analyte concentration ranges; interactive experimental design from database results to guide temperature programmed operation

Activities to be Emphasized in FY01:

- Design of one or more demonstration problems (with DoE input)
- Selection of candidate films for demonstration arrays, and investigation of level of film reproducibility
- Evaluative studies of devices and signal processing in demonstrations involving analyte mixtures
- Exploration of methods to enhance long-term operation

Information Access

Published Papers

1. R.Walton, C. Kendrick, B. Panchapakesan, D. DeVoe, R. Cavicchi and S. Semancik, "Processing Methods for Selected Area Film Deposition and Preparation on Microsensor Platforms Using Thermal and Potential Control", *Digest of the 10th International Conference on Solid-State Sensors and Actuators*, Sendai, Japan, Vol. 1, June 1999, pp. 676-679.
2. B. Panchapakesan, D. L. DeVoe, R. E. Cavicchi, R. M. Walton and S. Semancik, "Micromachined Array Studies of Tin Oxide Films: Nucleation, Structure and Gas Sensing Characteristics", Proceedings of the MRS (Spring 1999) Vol. 574, pp. 213-218.
3. R. E. Cavicchi, S. Semancik, R. M. Walton, B. Panchapakesan, D. L. DeVoe, M. Aquino-Class, J. D. Allen and J. S. Suehle "Microhotplate Gas Sensor Arrays", Proc. SPIE International Symposium on Industrial and Environmental Sensing (Boston, MA, 9/17-22/99) Vol. 3857, pp. 38-49.
4. R.Walton, R. Cavicchi, S. Semancik, B. Panchapakesan, D. DeVoe, M. Aquino-Class, J. Allen and J. Suehle, "Solid State Gas Microsensors for Environmental and Industrial Monitoring", Proc. SPIE International Symposium on Industrial and Environmental Sensing (Boston, MA, 9/17-22/99) Vol. 3853, pp. 254-261.
5. J. Ding, T. Mc Avoy, R. Cavicchi and S. Semancik, "Quantification of a Single Component Gas in Air with a Microhotplate Gas Sensor Using Partial Least Squares Techniques", Proc. SPIE International Symposium on Industrial and Environmental Sensing (Boston, MA, 9/17-22/99) Vol. 3856, pp. 162-170.

Presentations

14 presentations, on work that was funded by DoE, and by NIST

Web Access

Information relating to our microsensor program can be found at http://www.nist.gov/chemsensors

Millimeter-Wave Measurements of High Level and Low Activity Glass Melts

Project ID: 65435

Dr. Paul P. Woskov, Massachusetts Institute of Technology

Research Objective

The goals of the research effort are to develop new robust diagnostic tools for glass melt monitoring in a high-temperature, corrosive, radioactive environment, and to advance glass melt chemical modeling to make possible real-time melt characterization via the new sensor capability. Millimeter-wave technology will be applied to the simultaneous measurement of temperature, conductivity, and viscosity for the first time. This new sensor technology will make possible better process control to improve reliability and efficiency of waste glass melters. Also, it will provide new data for bridging the gap between theoretical glass melt models and their relationship to melter performance. The work is closely coupled to the needs of the Defense Waste Processing Facility (DWPF), West Valley Demonstration Project (WVDP), and vitrification efforts at Hanford, Oak Ridge, and Idaho sites. This research is a collaboration between the Massachusetts Institute of Technology (MIT) Plasma Science and Fusion Center (PSFC), the Pacific Northwest National Laboratory (PNNL), and the Savannah River Technology Center (SRTC).

Research Progress and Implications

As of the second year good progress has been made in parallel on the various research objectives. Laboratory experiments at MIT have established the feasibility for real-time monitoring of all three parameters, temperature, conductivity, and viscosity. Also a new capability for molten glass density measurements at high-temperature was discovered. A key milestone in the second year was a meeting[1] with Tank Focus Area representatives at MIT on December 7, 1999 to discuss monitoring priorities and the transfer of this technology to the TFA. Viscosity measurement was identified as the most important need. Experiments following this meeting demonstrated a strong correlation between millimeter-wave molten glass displacement measurements and viscosity. These results imply that robust new sensors for characterizing glass properties *in situ* are possible for improving control of present and future generation melters. Progress is briefly summarized below by the collaborating institution that led the particular developments described.

PSFC (MIT): Experiments continued in the second year with millimeter-wave instrumentation at a frequency of 137 GHz on a laboratory furnace. In collaboration with PNNL a number of different waveguide types, materials, and sizes were tested for interfacing the remote electronics with the molten glass. The two main waveguide types were internally corrugated metal guides and internally smooth non-conducting guides, which can propagate the efficient HE_{11} mode. Inconel 690 was used for testing waveguides of the first type. Performance was good for up to 1150 °C but repeated use up to 1180 °C showed degraded performance due surface corrosion. Silicon carbide (SiC) and mullite ($3Al_2O_3 \cdot 2SiO_2$) were used to test waveguides of the second type. Though tests of high resistively SiC samples indicated this would make a good dielectric waveguide, the vendor for this material could not produce a high resitivity tube. Mullite on the other hand proved to be a very effective millimeter-wave waveguide material. It has been successfully used in repeated measurements to 1300 °C, both above and immersed into the molten glass with millimeter-wave transmission efficiencies of 93% in the present setup. The implication of this result is that robust access for millimeter-wave sensors into glass melters in an oxidizing environment is now well established.

A number of experimental runs with two different Hanford glasses have been carried out to develop the measurement techniques using both the Inconel and mullite guides. The measurement of

temperature and emissivity has been shown. The feasibility of viscosity measurements has also been established by sealing the waveguide with a window and connecting to a pressurized source of gas. The rate of flow of molten glass in the waveguide, in response to a pressure transient, has been shown to be dependent on glass viscosity. Furthermore, the magnitude of the liquid glass displacement for a given pressure is dependent on the liquid density. Data for a Hanford glass mix over a temperature range of 1000 - 1300 °C and corresponding viscosity range of 3,000 – 100 Poise has been acquired. Millimeter-wave molten glass turbulence is a significant feature at viscosity below 200 Poise. The viscosity measurement development work is currently ongoing to optimize measurement methods and techniques, and to obtain additional data on other glasses.

PNNL: Work at PNNL has focused on molten glass conductivity – chemistry relationships and supporting the experiments at MIT.

Electrical Conductivity: A high-accuracy coaxial-cylinders technique was adapted successfully to measure the conductivity of waste glass melts. Characterization of 3 Hanford glasses, 6 DWPF glasses, and 5 privatization glasses was completed. Conductivity of the 2 Hanford glasses and 1 DWPF glass was predicted using 1) first-principle process-product model, developed by Jantzen[2] and 2) empirical mixture models, developed by Hrma et al.[3] . Preliminary comparison of the predictions with the measured value showed promise for developing a good conductivity-chemistry relationship. Further development of this relationship is in progress.

Redox: The coaxial-cylinders technique was modified to include a stabilized zirconia reference electrode. This modified probe will be used to measure redox of the waste glass melts from the glass test matrix, using square-wave voltammetry. A modified version of Rapidox, probe will also be used. These results will be compared.

SRTC: Research at SRTC has focused on the development of an advanced "Process Model" based control system that would use information from *in situ* measurements of millimeter wave emissions from molten glass to determine the glass composition. The current process control strategy in the Defense Waste Processing Facility uses analytical measurements of the compositions of the feed components along with an assessment of the uncertainties in the analysis and in the process variables such as batch volumes to ensure that acceptable glass will be made downstream from the blend tank. This is a feed forward control strategy. Direct measurement of product composition offers the possibility of feed back process control where the measured product properties are used to optimize the control of the system. The millimeter wavelength radiation profile from the glass would be fed into a process model that accounts for uncertainties in the measurements and system response to minimize the amount of frit added to the glass. Unlike the current control strategy, the new control strategy uses information about the composition of the blend tank, the melter feed tank, and glass already in the melter to determine an optimum glass blend. The glass produced by this strategy is potentially a more nearly optimal composition than it is currently possible to obtain. Future work will focus on quantifying the benefits of a feedback control system and will also consider measurements in the presence of disturbances such as temperature fluctuations to the system.

1 Participants: Bill Holtzcheiter, Frank Thomas III, *from SRTC;* Tom Thomas, *from INEEL*; Glenn Bastiaans, *from Ames*; S. K.. Sundaram, *from PNNL*; Paul Woskov, John Machuzack, Kamal Hadidi, and Paul Thomas, *from MIT.*

2 C. M. Jantzen, "First Principles Process-Product Models for Vitrification of Nuclear Waste: Relationship of Glass Composition to Glass Viscosity, Resistivity, Liquidus Temperature, and Durability," pp. 37-51 in Nuclear Waste Management IV, Editor: G. G. Wicks, D. F. Bickford, L. Roy Bunnell, Ceramic Transactions, Volume 23, The American Ceramic Society, Westerville, Ohio, USA, 1991.

3 P. R. Hrma, G. F. Piepel, P. E. Redgate, D. E. Smith, M. J. Schweiger, J. D. Vienna, and D. –S. Kim, "Prediction of Processing Properties for Nuclear Waste Glasses," Ceramic Trans. 61, 505-513 (1995).

Improved Analytical Characterization of Solid Waste-Forms by Fundamental Development of Laser Ablation Technology

Project ID: 55318

Dr. Richard E. Russo, Lawrence Berkeley National Laboratory

Research Objectives

Laser ablation (LA) with inductively coupled plasma mass spectrometry (ICP-MS) has been demonstrated as a viable technology for sample characterization within the EM complex. Laser ablation systems have been set up at the Hanford Site, Savannah River Plant, the Pu immobilization program (MD), Los Alamos, and at numerous other DOE facilities. Advancement of this technology is warranted to guarantee accuracy of analysis for the diversity of complex EM samples. This EMSP research endeavors to understand fundamental laser-ablation and ICP-MS detection characteristics, to ensure accurate and sensitive analytical characterization for EM waste-site samples. The difficulty in characterization of EM waste samples is that matrix-matched standards are not available. ICP-MS instrumental calibration must be performed with a series of standards. The sample-matrix will influence the ablation process, such as an amount of ablated mass, elemental fractionation, particle size distribution and particle transport characteristics, and ICP-MS response. If matrix-matched standards existed, the quantity of mass, degree of fractionation, and particle transport would be the same for standards and samples; hence, accuracy of analysis would be guaranteed. In contrast, for most EM samples in which standards are not available, accuracy can only be accomplished through knowledge of the laser ablation processes.

The following issues were studied to improve applicability of laser ablation for accurate and sensitive characterization of EM solid samples:

1. Effects of particle size distribution on ICP-MS signal intensity.
2. Effects of sample matrix on dry ICP plasma.
3. ICP-MS optimization for laser ablation sampling.
4. Space charge effects on ICP-MS detection.
5. Importance of matrix matched standards.

Research Progress and Implications

1. Effect of particle size distribution on ICP-MS signal intensity.

Problem significance and relevance to the DOE material characterization needs.

The amount of mass removed from the sample per each laser pulse, entrainment of particles in the chamber, transport of particles through the tubing, and atomization and ionization of particles in the ICP all influence the efficiency of the LA-ICP-MS system. Furthermore, entrainment efficiency plays a crucial role in analysis of radioactive materials where chamber and transfer tube contamination should be minimized as much as possible.

The relation between laser-generated particles and ICP-MS signal intensity was investigated using single pulse laser ablation sampling of Savannah River Site (Vitrification Facility) prototypical waste-glass samples. The particle size distribution was measured using an optical particle counter for different laser ablation conditions. For single pulse laser ablation, fewer particles were produced for the first pulse than successive pulses that repeatedly irradiated the same surface location. ICP-MS signal intensity corresponding to the first pulse was lower compared to successive pulses. Size distribution of laser-generated particles changed with laser power density and beam diameter. Laser

power density of about 0.4 – 0.5 GW/cm^2 was found to be a threshold value, over which particle size distribution changed. Laser beam diameter was the more influential parameter than power density in efficient particle generation. The onset of ICP-MS intensity time profiles decreased as more large particles were generated, indicating particle-size dependent separation within an ablation chamber. ICP-MS intensity data were calibrated with respect to the particle mass entering the torch. Particle entrainment efficiency of the LA-ICP-MS system was found to be a strong function of laser power density (Figure 1). Particle entrainment efficiency decreases from about 25% at low laser power density to less that 5% at high power density. These data demonstrate that at high laser power density, more mass will be lost, leading to contamination of the ablation chamber and particle-transfer tubing.

2. Matrix effects on dry ICP plasma conditions.

Problem significance and relevance to the DOE material characterization needs.

Analytical performance characteristics of LA-ICP-MS are determined by the ICP operating parameters. Different quantities of mass entering the ICP plasma during laser ablation of samples and standards are not uncommon. For accurate chemical analysis of laser ablated mass with ICP-MS, the ablated mass entering the ICP must not perturb the plasma conditions. Thus, studies of matrix loading in the ICP are an important step in developing LA-ICP-MS for DOE applications.

The chemical matrix effect on the plasma conditions was studied by optically measuring the ionic to atomic spectral line intensity ratios in the ICP. The values of these ratios depend on plasma

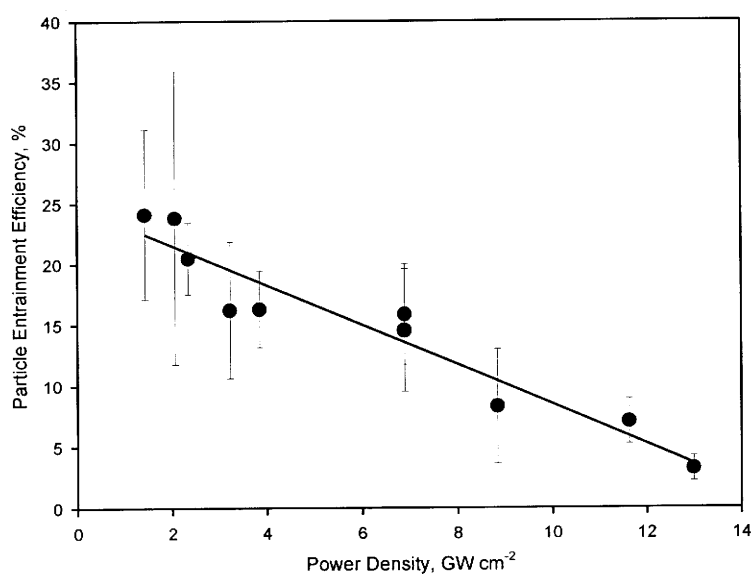

Figure 1. Particle transport efficiency in LA-ICP-MS as a function of laser power density. Laser was operated in a single pulse mode.

temperature and electron number densities. Electron number densities and plasma temperature are important parameters determining particle vaporization and ionization efficiency. It was found that the matrix effect using laser ablation solid sample introduction and solution nebulization is different, due to the different nature of wet and dry ICP plasmas. Figure 2 illustrates a matrix effect by showing the percentage ratio change of Zn ionic to atomic emission lines in the ICP as a function of a relative matrix amount. Effect of CaF_2, MgO, and Li_2CO_3 matrices are compared. In these experiments,

laser ablation was performed in two chambers simultaneously. In the first test chamber, laser ablation of Zn was conducted at constant energy conditions. Laser ablation of matrix was done in the second chamber.

Li_2CO_3 matrix showed no observable change in the plasma conditions while CaF_2 and MgO showed a drastic change in plasma conditions. In general, it was determined that Ca has more pronounced matrix effect on ICP plasma than other easy ionizable elements (such as Li, Na, and K). The chemical composition of the waste-site sample must be preliminary known to ensure accurate analysis. Preliminary knowledge of sample composition also is warranted with solution digestion. Laser ablation still benefits by not having to digest the sample and generate additional waste.

3. ICP-MS optimization for laser ablation sampling.

Problem significance and relevance to the DOE material characterization needs.

ICP-MS optimization will influence sensitivity of analysis. Instrumental parameters for laser ablation and liquid nebulization sample introduction are expected to be different. Fundamental understanding of conditions that govern ICP-MS optimization will allow one to directly analyze solid materials without using liquid standards.

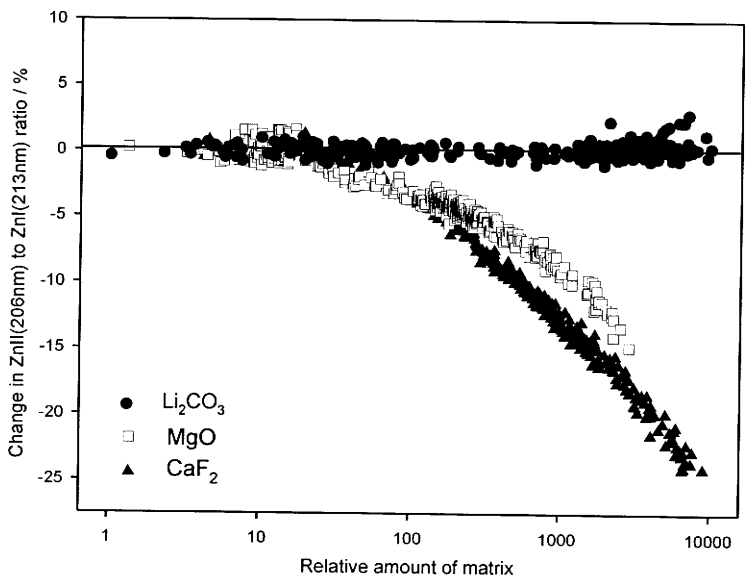

Figure 2. Percentage ratio change of Zn ionic to atomic emission lines in the ICP as a function of a relative amount of CaF_2, MgO, and Li_2CO_3 matrices.

ICP-MS optimization was done during steady state laser ablation of various samples, including Zr metal and NIST 610 glass. Ar gas flow rate, that carries ablated particles into the ICP, must be optimized: first, to provide favorable vaporization and ionization conditions in ICP and second, to minimize particle losses inside a chamber and transfer line. Typical Ar gas flow rates used in laser ablation work are in the range of 0.7 – 1.0 L min^{-1}. These flow rates are governed primarily by ICP ionization requirements. Figure 3 shows ICP-MS signal intensity as a function of Ar gas flow rate. Typical dependence was observed when flow rate was varied from 0.1 to 1.4 L min^{-1} (bottom axis). In contrast, when ICP conditions were maintained constant, keeping the total flow into the ICP the same (by mixing Ar gas flow through the chamber with an additional flow at a base of an ICP torch), ICP-MS signal intensity did not change significantly in the range of carrier flows of 0.1 – 0.9 L min^{-1}. These data demonstrate that central channel flow rates are determined by ICP plasma conditions and not by particle transport properties. Flow rate of 0.1 L min^{-1} is as efficient in transporting ablated mass as much higher 0.9 L min^{-1} flow.

ICP-MS ion-optics optimum voltages were found to be significantly different for dry and wet ICP plasmas. Two orders of magnitude improvement in sensitivity was observed when the ICP-MS was tuned for solid sampling conditions. ICP conditions, such as temperature and electron number density, determine ICP sampling through the interface and, hence, total ion current through the ion optics. Based on optically measured ICP temperature and electron number densities, total current for sampling from dry and wet plasmas was compared. For the typical operating conditions ion current for sampling from wet plasma is only in the range of 0.2 – 1.0 μA, whereas for sampling from dry plasma the current is about 10 μA. This is believed to be determining factor in optimum ion-optics settings. Furthermore, the average ion kinetic energies for the dry plasma is about 5 – 6 eV lower than for the wet plasma.

4. Space charge effects in ICP-MS.

Problem significance and relevance to the DOE material characterization needs.

ICP-MS matrix effects, known as space charge effects, can significantly contribute to analytical uncertainties, especially when light elements have to be determined in a background of a heavy-element matrix. For example, determining alkali and/or alkali-earth elements in Pu or U oxides will cause space charge effects, suppressing light-elements response. In this work we qualitatively investigated space charge effects in the ICP-MS and their influence on instrumental operating conditions.

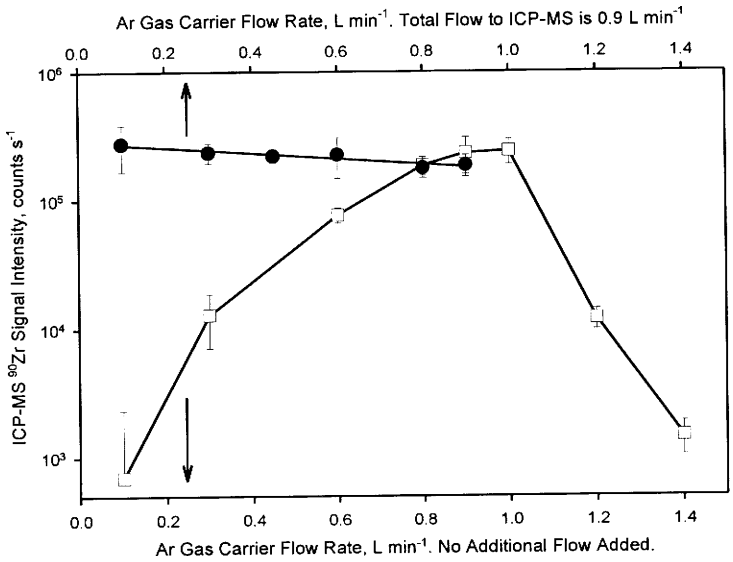

Figure 3. ^{90}Zr ICP-MS signal intensity as a function of a carrier Ar gas flow rate during repetitive ablation of Zr metal with no additional flow (bottom axis) and with various flow rates through the ablation chamber, but fixed total flow rate of 0.9 L min^{-1} into the ICP (top axis).

The ICP-MS interface was modified using a three-grid ion energy analyzer. This system allows for kinetic energy of sampled ions to be measured. The principle behind such measurements is that ion transmission through an analyzer drops when the applied voltage matches the ion kinetic energy. As a result, stopping curves can be obtained. Figure 4 compares stopping curves for Ba and Li at different Ar gas flow rates. It can be seen that Ba stopping curves are unaffected by Ar gas flow rate. In contrast, Li curves have different shape at different flows. At high flow rates of 1.0 and 1.2 L min^{-1} stopping curves resemble those for Ba. When flow rate was decreased to 0.7 L min^{-1} this behavior changed. As stopping voltage increases, Li signal decreases but at slightly higher grid

potentials, indicating some increase in Li kinetic energy as flow was decreased. At grid potential of about 7 – 8 V Li signal intensity sharply increases and tails off as potential increases further. The sharp signal increase becomes more significant as flow rate was further reduced to 0.5 L min^{-1}. It also can be noted that at this Ar gas flow rate, Li ions have higher kinetic energies. As flow rate was reduced to 0.3 L min^{-1}, only backgound Li levels were detected (note that the data presented in Figure 4 were normalized to the highest signal intensity for each curve). At grid potential of about 9 V Li counts increase and then slowly decrease as potential was further increased.

Space charge effects have more influence on light masses. After the second expansion stage, electro-neutrality of the beam can be lost. Positive potential applied to the extraction lens facilitates this process. As a result of charge separation, ion-ion interactions push highly mobile light elements to the outer regions of the beam, whereas heavy elements stay on axis. Space charge effects are more severe as ion current through the skimmer cone increases. As was determined, ion current depends on plasma operating conditions and decreases from about 200 µA to about 20 nA as flow rate was increased from 0.4 to 1.4 L min^{-1}. This explains anomalies in Li stopping curves. At low flow rates and high ion currents, space charge effects are strong. In contrast, significance of space charge diminishes as flow rate increases (low ion currents). As grid potential increases, the total ion current through the energy analyzer drops. Because light elements are concentrated at the outer zones of the ion beam they can gain energy upon collisions with heavy ions as the later are repealed by the positive potential at the grid. This will allow for light ions to gain enough energy to pass through the energy analyzer.

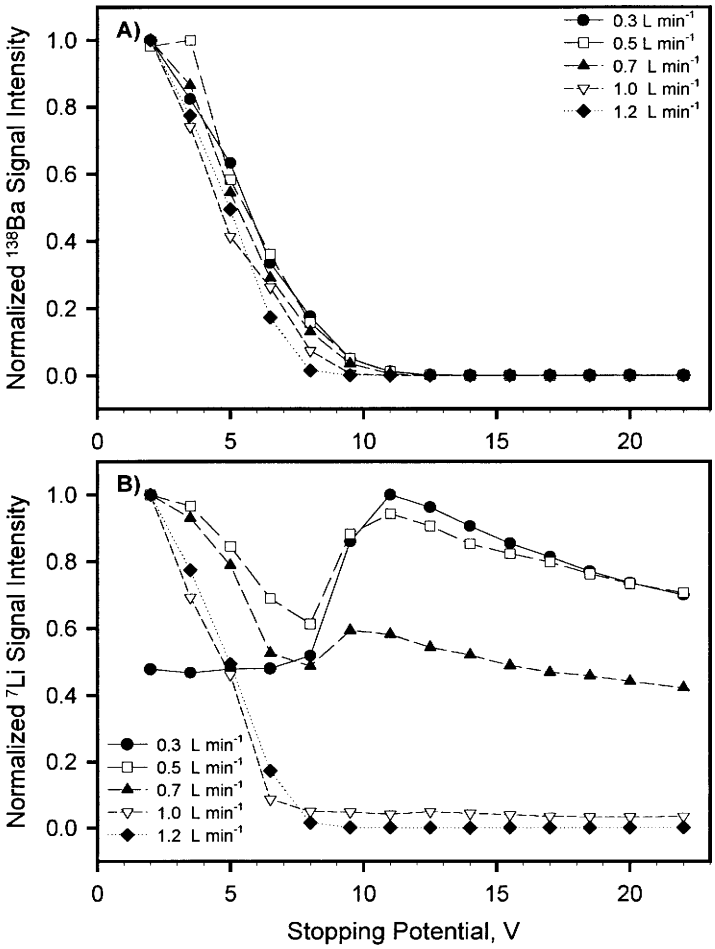

Figure 4. ^{138}Ba(a) and ^{7}Li (b) stopping curves at different flow rates (given in legends).

The research performed for this EMSP project clearly demonstrates that a fundamental understanding of laser ablation and ICP-MS operating conditions can lead to enhanced sensitivity and guarantee accuracy of analysis for characterization applications within the EM program. LA-ICP-MS technology provides significant cost savings for the EM program by eliminating sample digestion procedures, eliminating additional waste, and ensuring safety of personnel. This FY99 EMSP effort clearly demonstrated that the chemical matrix effect is a remaining area that needs to be understood for achieving accurate analysis without matrix-matched standards. Eliminating the need for matrix-matched standards would be a major breakthrough in the use of laser ablation for complex waste-site samples.

Information Access

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Laser Ablation ICP/MS calibration based on binary Cu/Zn alloy standards, O.V. Borisov, X.L. Mao, and R.E. Russo, *accepted in Spectrochimica Acta B, March 1999.*

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Optical Emission Spectroscopy Studies of Ablated Material on Dry Inductively Coupled Plasma Conditions, A.C. Ciocan, X.L. Mao, O.V. Borisov, and R.E. Russo, *COLA, July 1997, Asilomar CA.*

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Fundamental and Applied Aspects of Laser Ablation for Chemical Analysis, Frontiers in Chemistry Lecture Series, Wayne State University, April 1999 (Invited).

Particle Generation and Transport During Laser Ablation Sampling for Chemical Analysis, R.E. Russo, S.H. Jeong, X.L. Mao, O.V. Borisov, and J. Yoo, 25th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), October 1998, Austin, TX (INVITED).

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Laser-Ablation Sampling with ICP/AES and ICP/MS: Fundamental Issues to Improve Analytical Applications, R.E. Russo*, Society of Applied Spectroscopy California Section Meeting, September 1998, Fremont, CA* (INVITED).

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Laser Ablated Mass Influence on the Properties of the ICP, R.E. Russo, X.L. Mao, A.C. Ciocan, and B.V. Borisov, *Twenty-Fourth Annual FACSS Meeting, October 1997, Providence, RI* (Invited).

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Optical Emission Spectroscopy of the Influence of Ablated Material on Dry Inductively Coupled Plasma Conditions, A.C. Ciocan, X.L. Mao, O.V. Borisov, and R.E. Russo, *COLA 97, July 1997, Asilomar CA*.

Thermospray Mass Spectrometry Ionization Processes Fundamental Mechanisms for Speciation, Separation and Characterization of Organic Complexants in DOE Wastes

Project ID: 59978

Dr. John E. Caton, Oak Ridge National Laboratory

Research Objective

The overall objective is to develop and enhance our understanding of chemical equilibria for major organic complexant species (chelators, chelator fragments, small organic acids and their products) in multi-component aqueous matrices such as the mixtures of DOE stored wastes. To progress toward this objective, organic complexants must be separated and speciated in mixutres of high ionic strength. HPLC employing zirconia-based stationary phases is being studied in order to understand the separation requirements for organic complexants and the products formed by complexants with metals in complex aqueous mixtures. Separated complexant species will then be characterized using positive and negative ion thermospray mass spectrometry (TSMS). The final goal is to develop the analytical capability needed to define chemical concentration and equilibria for complexant species in DOE waste streams.

Research Progress and Implications

Significant progress during the past twenty-eight months of the 3-year project has been made in understanding the effectiveness of zirconia-based stationary phases for separating complexing agents such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepetaacetic acid (DTPA), citrate and oxalate. Each of these complexing agents has been used to solubilize radioactive metals from spent fuel rods and nuclear processing equipment, and now are components of high-level alkaline tank waste. Other chelators being studied are ethylenediamine-N,N_-diacetic acid (EDDA), imidodiacetic acid (IDA), N-2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) and N-(2-hydroxyethyl imonodiacetic acid (HEIDA), which may be present as degradation products and are potential complexers of strontium and cesium, the primary fission products found in DOE tank waste.

Separation investigation initially employed bare zirconia particles with an average diameter of 3 µm as the stationary phase in HPLC separation. The zirconia is known to have Lewis acid sites that coordinate hard Lewis bases such as carboxylates very strongly. The stationary phase also exhibits Brönsted acid/base character that can provide fixed charge sites for anion or cation exchange depending on the pH of the eluant. However, it is the coordination chemistry of zirconia that has been exploited to separate the chelators. A variety of elution conditions were tested. Two approaches were applied. The first used gradients of increasing hydroxide or increasing fluoride concentration to provide competing ligand to displace the complexants. However, even at very high pH, the complexants were either irreversibly sorbed or the band width of complexant profiles was so great that this approach was deemed impractical. In a second approach low pH gradients or low pH buffers with a gradient of increasing ionic strength of acetate or fluoride were used. The rationale was that at low pH the chelators would be partially protonated in free solution and the formation constant for the zirconium-chelator complexes would be less favorable, allowing elution of the complexants. Results indicate that if the pH is too low or if the fluoride concentration is greater than 10 mM, the chelators elute as a group with virtually no retention. Even with moderate pH or fluoride gradiants, the solutes do not elute in well-formed bands, presumably due to very slow desorption kinetics.

In contrast, work with zirconia coated with quaternized polyethyleneimine (QPEI) effected the separation of IDA, NTA and EDTA quite well under a variety of elution conditions. The separation

of these complexants on QPEI-zirconia falls into three general groups: 1) IDA, EDDA, and HEIDA are weakly retained; 2) NTA, EDTA, HEDTA, and DTA show moderate retention and can be separated under a variety of eluting conditions; and 3) oxalate and citrate are strongly retained and can be eluted with gradients in pH or bicarbonate. Further investigations are being pursued to optimize complexant separation on QPEI-coated zirconia.

HPLC separations followed by thermospray mass spectrometry have been utilized to develop positive ion mass spectra of organic complexants related to EDTA. These spectra have been defined at different source temperatures in water:methanol solvent systems containing different buffering components. Mass spectra show a peak at mass $[M+1]^+$ when vaporized from solvent media at low pH. As the pH increases the relative amount of mass $[M+1]^+$ appears to decrease in favor of a mass at $[M + adduct]^+$. This tendency to form an adduct in the gas phase can be related to the relative proton affinity of these complexants in the vapor phase. A lower proton affinity in the vapor phase should be consistent with greater acidity in the solution phase. Such characteristics may aid in defining behavior in solution. Accordingly interpretations of TSMS spectra should be useful in the characterization of DOE mixed waste solutions.

As a caveat to the study of bare zirconia as an HPLC stationary support, the material is also being evaluated as a sorbent for the selective removal of complexants or complexed metals at the head end of a waste treatment flowsheet. To simulate a waste treatment process, batch tests were performed in which bare zirconia was added to process water containing ^{90}Sr and ^{137}Cs in the presence and absence of citrate. Results indicate that neither the radionuclides nor citrate were sorbed on bare zirconia. Batch tests simulating high alkaline tank wastes containing EDTA still need to be performed.

Planned Activities

Within the remaining eight months of the project the following activities will be accomplished: 1) optimization of chelator separation on QPEI-coated zirconia; 2) conclude predictive capability of proton affinity (or gas phase acidity from TSMS characteristics; 3) complete TSMS studies of known chemical species of complexants and metal ions; 4) detail project results in a manuscript for the open literature. [There will be a no-cost extension of the chromatography development at the University of Minnesota in order to accommodate the availability of a post-doctoral research worker.]

Information Access

Results from these investigations will be published in the open literature. At this point in time the following presentations have been given at national scientific meetings:

1. "Separation and speciation of organic complexants in DOE wastes using HPLC on zirconia-based stationary phases and thermospray mass spectrometry". American Chemical Society, Fall Meeting, New Orleans, LA, August 22-26, 1999.
2. "HPLC separation of chelating agents on quaternized polyethyleneimine coated zirconia". Eastern Analytical Symposium, Somerset, NJ, November 16, 1999.

f-Element Ion Chelation in Highly Basic Media

Project ID: 54595

Dr. Robert T. Paine, University of New Mexico

Research Objective

High-level radioactive waste (HLW) generated in the DOE complex is stored in tanks at several sites, but predominantly it is found at the Hanford reservation. Much of the material has been exposed to high pHs, consequently the waste exists in a complex, poorly understood mixture of solids, gels and solutions. The final waste remediation plan may involve chemical separation of fractions and a suitable, well developed molecular chemistry basis for performing these separations is not available. Indeed, the fundamental chemical behavior of most radioactive nuclides in basic media is not known.

The goal of this project is to undertake fundamental studies of the coordination chemistry of f-element species in basic aqueous solutions containing common waste treatment ions (e.g., NO_3^-, CO_3^{2-}, organic carboxylates, and EDTA), as well as new waste scrubbing chelators produced in this study. The experimental agenda includes:

1. Studies of the speciation of Sr and Ln ions in basic solutions with and without common counterions;
2. Preparations of new multifunctional ligands that may act as strong, ion-specific chelators for Sr and/or Ln ions in basic media; and
3. Studies of the coordination and dissolution behavior of oxide-hydroxide species, as well as in insoluble sols, gels, and precipitates in combination with new chelating ligands.

It is anticipated that this coordination chemistry will facilitate the design of advanced separation schemes required for handling the complex waste matrices found at the Hanford HLW facility.

Research Progress and Implications

As of 6/1/99 the following advances have been realized.

1. Hydrolysis Chemistry

   We have continued our study of the pH dependence of the hydrolysis of Sr(II), Y(III), La(III), Nd(III), and Er(III) by use of pH titrations and nephelometry. Particular attention was given to determining the pH for the onset of hydrolysis as well as the kinetics of particle growth at onset. The pH values for hydrolysis onset generally agree with related data in the literature. The pH shifts in hydrolysis onset as a function of counterion have also been studied as a function of ions typically present in waste media (e.g., NO_3^-, Cl^-, acetate, oxalate), as well as known chelating anions. As expected, many of these ions cause significant shifts in the pH for hydrolysis onset due to competing association equilibria. The hydrolysis onset shifts caused by phosphonic acid chelators have also been surveyed. Dramatic shifts are encountered in some cases comparable to those observed with EDTA. For example, for La(III) the pH shifts are typically 6 pH units. Some attention was also given this year to studies of solutions containing several metal ions. This work was undertaken to assess the influence of a “matrix” of metal ions on the hydrolysis of a single ion. The studies completed to date are qualitative in nature and the results are being used to design more quantitative studies in the future. The future studies will access the cross-behavior of ions in “simulant” waste compositions suggested by Task Focus area personnel.

In related work, we continued studies of the dissolution properties of lanthanide oxide-hydroxide precipitates with complexing anions. It is found that several new phosphonic acids are very active at precipitate dissolution. In support of this work, we have structurally analyzed the precipitates and the dissolution complexes by use of solution and solid-state NMR and we have isolated a number of complexes in the solid state and determined their molecular structures.

2. New Complexant Development

Considerable effort has been given to this activity in the last year. First of all the coordination chemistry of ligands 1 – 5 reported last year was explored in support of understanding how these ligands bind to lanthanide ions as they are dissolved from basic sludges. The molecular structures of $Er(1^-)_3$ (1) was determined and 1 was found to coordinate both in its mono anionic form and as a neutral ligand. The nature of the bonding is consistent with complete replacement of oxo and hydroxo groups from the metal center. A derivative ligand (1') of 1 in which another methylene group is added between the phosphonic acid group and the pyridine ring was prepared. This ligand forms 3:1 complexes with Nd(III) in which each ligand is bound to a metal ion in a bidentate fashion and also bridge bonds to a second metal center. The result is a polymeric structure. The functional analog of ligand 2 has been prepared and the coordination chemistry has been studied. In each case the date, molecular structure determinations show the molecule binds in a tridentate fashion to one metal center and then bridge bonds to two more metal centers giving rise to a polymeric structure.

The implications of these coordination chemistry studies are several. First, they shed light on the powerful dissolution properties of the ligands. Clearly, the strong ligand-metal interactions drive the metals out of their otherwise stable oxide-hydroxide structures. The solid state structures reveal new chelation designs that would be worth pursuing and they point to directions for fruitful decontamination activities.

Planned Activities

We have requested and have been granted a no-cost, one year extension to this grant. During this last year we will pursue additional efforts in chelator design for dissolution agents and we will test the effectiveness of the new ligands in simulant insoluble waste systems.

Actinide-Specific Interfacial Chemistry of Monolayer Coated Mesoporous Ceramics

Project ID: 65370

Dr. Glen E. Fryxell, Pacific Northwest National Laboratory

Dr. Tom S. Zemanian, Pacific Northwest National Laboratory
Dr. Ken M. Kemner, Argonne National Laboratory
Dr. Ken Raymond, University of California at Berkeley

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) management at several DOE sites.

Research Progress and Implications

This report summarizes work after 1.5 years of a 3-year project. Selective isolation of actinides from a complex mixture is anticipated to increase assay accuracy, speed up assay turnaround, reduce waste volume (and costs), and enhance decontamination efficiency and safety. In Year 1, we developed powerful new SCF synthesis methods that significantly enhance our capabilities in the production of SAMMS; we developed a series of first generation sorbent materials and evaluated their capabilities using lanthanide models; and we developed a novel anion sequestration strategy. In Year 2, we have extended our SCF methods to include SC nitrogen (which has certain advantages over other SCFs); we have refined our interfacial ligand field to exploit chelators with extremely high affinity for the actinides; we have determined binding kinetics (3-5 minutes) using lanthanide models; we have started with competition experiments to evaluate competition by common competing metal cations; started to acquire actinide binding data; obtained detailed characterization of the binding of tetrahedral oxoanions to our anion SAMMS and applied these materials to the sequestration of pertechnetate.

Planned Activities

In Year 3, we intend to extend our actinide studies to include all of the actinides from Th through Am; we will 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

List publications and any other access to results (e.g., a Web page). http://www.pnl.gov/etd/product/samms/index.htm
http://www.acs.org/government/success/index.html

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"Self-Assembled Monolayers on Mesoporous Supports for Metal Separation" S. Mattigod, G. E. Fryxell, X. Feng and J. Liu* in " Metal Separation Technologies Beyond 2000: Integrating Novel Chemistry with Processing", edited by K. C. Liddell and D. J. Chaiko, published by The Minerals, Metals and Materials Society, pp. 71-79, **1999.**

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Actinide-Aluminate Speciation in Alkaline Radioactive Waste

Project ID: 65318

David L. Clark, Los Alamos National Laboratory

Dr. Nikolai N. Krot, Transuranium Element Laboratory

Research Objective

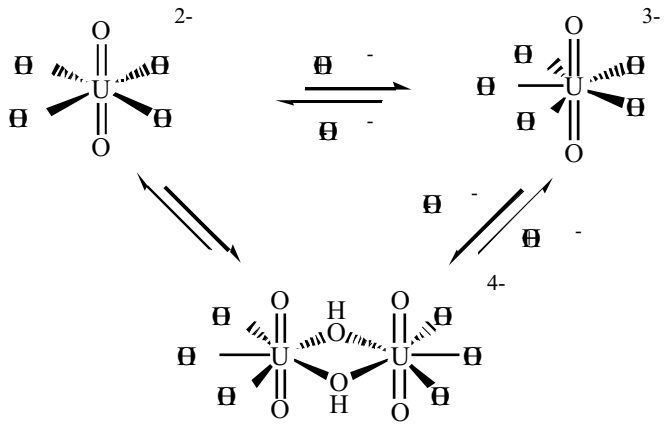
Highly alkaline radioactive waste tanks contain a number of transuranic species, in particular U, Np, Pu, and Am—the exact forms of which are currently unknown. Knowledge of actinide speciation under highly alkaline conditions is essential towards understanding and predicting their solubility and sorption behavior in tanks, determining whether chemical separations are needed for waste treatment, and designing separations processes. Baseline washing of tank sludges with NaOH solutions is being proposed to reduce the volume of HLW. Alkaline pretreatment of HLW will be needed to remove aluminum [as $NaAl(OH)_4$] because it significantly reduces the HLW volume; however, the aluminate ion [$Al(OH)_4^-$] enhances actinide solubility via an unknown mechanism. Thus, alkaline wash residues may require an additional treatment to remove actinides.

The results of this research will determine the nature TRU (U, Np, Pu, Am) speciation with aluminate anions under alkaline, oxidizing tank-like conditions. Specific issues to be addressed include solubility of these actinides, speciation in aluminate-containing alkaline supernatants, the role of actinide redox states on solubility, and partitioning between supernatant and solid phases, including colloids. Studies will include thermodynamics, kinetics, spectroscopy, electrochemistry, and surface science. We have already determined, for example, that certain high valent forms of Np and Pu are very soluble under alkaline conditions due to the formation of anionic hydroxo complexes, $AnO_2(OH)_4^{2-}$ and $AnO_2(OH)_5^{3-}$. The presence of aluminate ions causes the actinide solubilities to increase, although the exact species are not known. We are currently characterizing the high-valent TRU elements bound to oxo, water, OH^-, and $Al(OH)_4^-$, ligands under waste-like conditions. These waste-like conditions are in the range of 1-3 M excess hydroxide, ~0.2 M carbonate, ~0.5 M aluminate, for a total sodium of 2-4 M. Molecular structure-specific probes include Raman, multinuclear nuclear magnetic resonance (NMR), extended X-ray absorption fine structure (EXAFS), luminescence, optical absorption (UV-Vis-conventional and photoacoustic) spectroscopies. We anticipate that such new knowledge will impact on clean-up approaches to significantly reduce costs, schedules, and risks.

Research Progress and Implications

In the first one and one half years of the project we have determined the true role of aluminate [$Al(OH)_4^-$] anions in enhancing solubility of actinide ions. Last year we reported preliminary spectroscopic observations of a new actinide chemical species in the presence of aluminate anions under alkaline, waste tank-like conditions. We postulated that the aluminate anion acted as a ligand to uranium, and that the new compound was an actinide-aluminate coordination complex of high negative charge. More detailed studies aimed at identification of this new species revealed that it is actually a new dimeric uranyl species, and that there is no aluminate anion in the metal coordiation sphere. Rather, the data indicate that the aluminate acts as an electrolyte, and increases the hydroxide ion activity and hence the overall solubility via formation of $UO_2(OH)_5^{3-}$. In general, highly charged species are stabilized by high ionic strength. This will have a direct impact on sludge washing using

NaOH to remove aluminate ions from the system. Changes in the aluminate concentration effect the position of the equilibrium outlined below. Furthermore, we also find changes in aluminum chemistry based on the presence of uranium, including aluminate precipitation reactions under conditions where the aluminate anions should be solubilized.



Reaction Scheme

Planned Activites

The workscope for the first year was altered in order to proceed with an increased efficiency. A decision was made to limit the first year's studies to uranium in order to better characterize the equilibria identified in Scheme 1. This process has allowed us to map out the complex chemistry shown in Scheme 1 with a metal center having the most spectroscopic tags. The originally planned plutonium work is now beginning. Work will be performed to synthesize model complexes from non-aqueous solvents where the equilibria described above will no longer interfere. In addition, experiments designed to obtain crystals from aqueous solution will be performed under the conditions leading toward single species. Further studies in vibrational spectroscopy, including IR and Raman, along with ^{17}O- and ^{27}Al-NMR will be performed to studying the nature and thermodynamics of the equilibrium.

Information Access

A manuscript describing the spectroscopic data leading to the description of Scheme 1 above will be submitted for publication this summer.

Actinide Species in Alkaline Media

Project ID: 65398

Kenneth L. Nash, Argonne National Laboratory

Mark P. Jensen, Argonne National Laboratory
Andrew H. Bond, Argonne National Laboratory
Linfeng Rao, Lawrence Berkeley National Laboratory

Research Objective

Using a variety of different techniques, this program attempts to provide relevant fundamental data that will reduce the number of surprises (related to actinide behavior) that occur during sludge washing and tank waste processing. We are building upon the results of earlier fundamental studies of actinide chemistry in concentrated alkali (many conducted in Russia), on the analysis of tank wastes, and on earlier sludge-specific leaching experiments to gain an improved understanding of the relationship between sludge characteristics and actinide dissolution during proposed sludge washing procedures. A successful outcome for this research will be the generation of sufficient supporting information (both fundamental and empirical) that will enable more accurate prediction of the probability of actinide dissolution during the scrubbing of sludges from PUREX, REDOX, and $BiPO_4$ processes. We are studying the mobilization of tri-, tetra-, penta-, and hexavalent actinide cations from sludge simulants; trying to identify mineral phases that might control actinide solubility in sludge simulants; learning about associations between actinide cations and non-radioactive sludge components; investigating the solution-phase chemistry of actinide cations in concentrated alkali; evaluating the contribution of colloid transport to actinide mobility in sludge washes.

Research Progress and Implications

The work conducted in this project is designed to provide new fundamental information on the chemical behavior and speciation of uranium, neptunium, plutonium, and americium in simulated alkaline tank waste sludges and alkaline scrub liquors. Sludges representative of those generated during plutonium production have been prepared using appropriate combinations of chemical components of the various waste streams that contribute to the complexity of alkaline tank wastes. These sludges have been characterized by a variety of techniques prior to radionuclide uptake/dissolution tests. To date, we have investigated samples prepared using these sludges containing uranium and plutonium isotopes introduced in the oxidation states pertinent to process conditions at tracer concentrations. These tagged solids were then subjected to consecutive and parallel leaching procedures with increasingly aggressive reagents. The dual purpose of these initial experiments is to determine the potential for mobilization of actinide ions during sludge washing, and to characterize the associations between actinide ions and non-radioactive waste components being dissolved out. Alkaline washes generally do not mobilize much Pu but substantial amounts of U are leached under a variety of conditions. The more aggressive treatments with acid and chelating agents demonstrate correlations between actinide concentrations and the transition metal components of the sludge. Unidentified iron and manganese species (likely oxides) and phosphate appear to be important in controlling actinide solubilization. Parallel experiments examining the behavior of Np have recently been started. We have also begun electrochemical experiments focusing for the present on Np(V)/Np(VI) transitions. These experiments are providing new information on redox potentials of actinides in concentrated alkali, specifically investigating the influence of those chelating agents likely to be seen during sludge washing on oxidation-reduction potentials. Our most unexpected result to date

has been the relatively high concentrations of uranium mobilized during sludge washing. To the extent actinide cations behave similarly in a given oxidation state, this result may be of great significance for Pu and Np dissolution under oxidizing conditions.

Planned Activities

Ongoing and planned experiments include studies of the leaching behavior of Am, Np, (and as an added bonus, Sr) from the representative sludge materials. Actinide speciation (at macroscopic actinide concentrations) in the insoluble sludges will be examined using X-ray diffraction and synchrotron radiation techniques. Parallel studies will address the chemistry of actinide ions in alkaline solutions, principally those containing chelating agents, using the various techniques of electrochemistry. Some of this work is already underway. The remainder will commence within the next 5-6 months.

Information Access

An oral presentation has been made at the 11th Symposium for Separation Science and Technology for Energy Applications. Poster presentations have been made at the New Orleans and two at the San Francisco American Chemical Society meetings. Our poster at the Materials Research Society meeting in Boston, fall, 1999, won a poster award, marking it in the top 1% of all posters presented. Two research papers are in press.

Development of Fundamental Data on Chemical Speciation and Solubility for Strontium and Americium in High Level Waste: Predictive Modeling of Phase Partitioning During Tank Processing

Project ID: 54621

Dr. Andrew R. Felmy, Pacific Northwest National Laboratory

Dr. Gregory Choppin, The Florida State University
Dr. David A. Dixon, Pacific Northwest National Laboratory
Dr. James A. Campbell, Pacific Northwest National Laboratory

Research Objective

In this research program, Pacific Northwest National Laboratory (PNNL) and Florida State University (FSU) are investigating the speciation of Sr and Am/Cm in the presence of selected organic chelating agents (ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA), and iminodiacetic acid (IDA)) over ranges of hydroxide, carbonate, ionic strength, and competing metal ion concentrations present in high level waste tanks. The project is comprised of integrated research tasks that approach the problem of chemical speciation using macroscopic thermodynamic measurements of metal-ligand competition reactions, molecular modeling studies to identify structures or complexes of unusual stability, and mass spectometry measurements of complex charge/mass ratio that can be applied to mixed metal-chelate systems. This fundamental information is then used to develop thermodynamic models which allows the prediction of changes in chemical speciation and solubility which can occur in response to changes in tank processing conditions. In this way we can both develop new approaches that address fundamental problems in aqueous speciation and at the same time provide useful and practical information needed for tank processing.

Current strategies for reducing the total volume of radioactive tank waste requiring disposal at Hanford and other DOE sites call for the developmemt of methods to selectively dissolve and remove non-radioactive elements such as Al, P, and Cr while retaining or precipitating the radioactive elements, including Sr and the actinide elements, in the tank sludges. This partitioning between solids and precipitates is fundamentally dependent upon the chemical speciation of the elements present in the tank processing solutions. Of particular importance is separation of the radioactive and hazardous actinide elements and fission products from the sludges and supernatants, particularly from supernatants containing high concentrations of strong chelating agents which can act to solubilize the actinides and fission products as well as interfere with subsequent metal ion extraction processes. Specifically, the fundamental understanding of chemical speciation reactions gained from these studies is needed to propose methodologies for removal of Sr and Am/Cm from organic chelates present in high level tank waste, via competition, displacement or other reactions, without the need for the development of costly and potentially hazardous organic destruction technologies.

Research Progress and Implications

Beginning in October 1996, we initiated a research program on Sr and trivalent actinide speciation in these high ionic strength, strongly basic solutions in the presence of organic chelates and competing metal ions. These data on chemical speciation and solubility were then used to develop aqueous thermodynamic models, based upon the Pitzer equations, for describing the chemical behavior of these elements in high ionic strength electrolytes.

The studies proceeded in a systematic manner beginning with the effects of hydrolysis (hydroxide concentration) on the chemical speciation of Sr to high base concentration. This was followed by studies on the effects of carbonate complexation on Sr extending to high carbonate concentration. This completed the studies of the major inorganic complexants for Sr and formed the foundation for the organic chelate studies. Studies on the effects of the organic chelates EDTA, HEDTA, NTA, and IDA were then completed. The effects of only one competing metal, Ca, were studied. The studies on Ca also required studying the effects of hydrolysis and carbonate complexation on the speciation and solubility of Ca since these factors must also be known to unravel the effects of a competing metal ion. Following the completion of the studies on Sr, the studies on the trivalent actinide analog, Eu(III) were conducted. These studies included the effects of high base on the complexation of EDTA, HEDTA, NTA, and IDA. These studies were completed in 1999. No studies on the effects of competing metal ions on the speciation of the trivalent actinides were conducted. The following section gives a brief summary of much of this work.

Studies on Sr speciation

In order to unravel the speciation reactions of Sr in complex tank waste requires studies of speciation reactions in the presence and absence of chelators. Specifically, in these initial studies speciation reactions in four chemical systems: Na-Sr-OH-H_2O, Na-Sr-CO_3-H_2O, Na-Ca-OH-H_2O, and Na-Ca-CO_3-H_2O with and without added chelators were studied. The systems including Ca as well as Sr were studied because of the presence of large amounts of Ca in tanks waste and high affinity of Ca^{2+} for the organic chelators.

This combined experimental and modeling approach also resulted in an aqueous thermodynamic model for the Na-Ca-Sr-OH-CO_3-H_2O system valid to high concentration at 25°C. The first published values of the equilibrium constants for the formation of $Sr(CO_3)_2^{2-}$, and $Ca(CO_3)_2^{2-}$ aqueous species and of the solubility product of $Sr(OH)_2 \cdot 8H_2O$ were determined along with the necessary Pitzer ion-interaction parameters to model these chemical systems. In the development of the thermodynamic model, computational chemistry methods were used to provide unique insight into the aqueous speciation reactions. The molecular modeling results were used to help determine whether ion-interaction or ion pairing approaches were appropriate in the thermodynamic analysis, suggested the possible existence of higher carbonate complexes in solution, and provided at least some guidance as to the reasonableness of independently calculated equilibrium constants.

Following these studies, the effects of calcium, hydroxide, and carbonate on the displacement of Sr from four organic chelates: EDTA, HEDTA, NTA, and IDA were studied in solutions with high base and carbonate concentration. Increases in hydroxide were ineffective in removal of Sr from the chelators even at base concentrations as high as 6M. Increases in carbonate concentration were effective in displacing Sr from the weaker chelators IDA and NTA but not from the strongest chelators HEDTA and EDTA. Competition with other metal ions, in this case Ca under highly basic and carbonate conditions, was shown to effectively displace Sr from the strong chelating agents HEDTA and EDTA, depending upon the concentration of Sr and the competing metal ions. Further, under a wide range of conditions, predominant chemical equilibrium constraints, were identified that resulted in simple predictive models for aqueous Sr and Ca organic-chelate complexes which are independent of the ionic media and thus can be applied to conditions with widely varying electrolyte composition.

An example of the effect of metal ion displacement of Sr by Ca is given in Figure 1 for the $CaCO_3$-$SrCO_3$-EDTA system. In the absence of Ca, the added EDTA stoichiometrically complexes with Sr and solubilizes the solid strontianite. Upon the addition of Ca (as calcite) the strong affinity of Ca for EDTA results in stoichiometric complexation of the EDTA with Ca and effective displacement

of Sr from the EDTA into the solid strontianite. This effect reduces the solubility of Sr in these solutions by almost three orders of magnitude. Clearly, such metal ion displacement reactions must be well understood to predict the effects of the chelators on Sr complexation. This result also indicates that metal ion displacement, if properly understood and manipulated, may represent an acceptable alternative to costly and hazardous organic destruction technologies in reducing the impacts of organic chelates in tank processing, especially given the fact that the strongest chelators represent only a small fraction of the total organic carbon in tank waste.

The results of these studies have been published in the open literature and presented at national society meetings and conferences (Oakes et al. 2000; Felmy and Mason 1998; Felmy et al. 1998; Felmy et al. 1997a,b,c; Sterner et al. 1998).

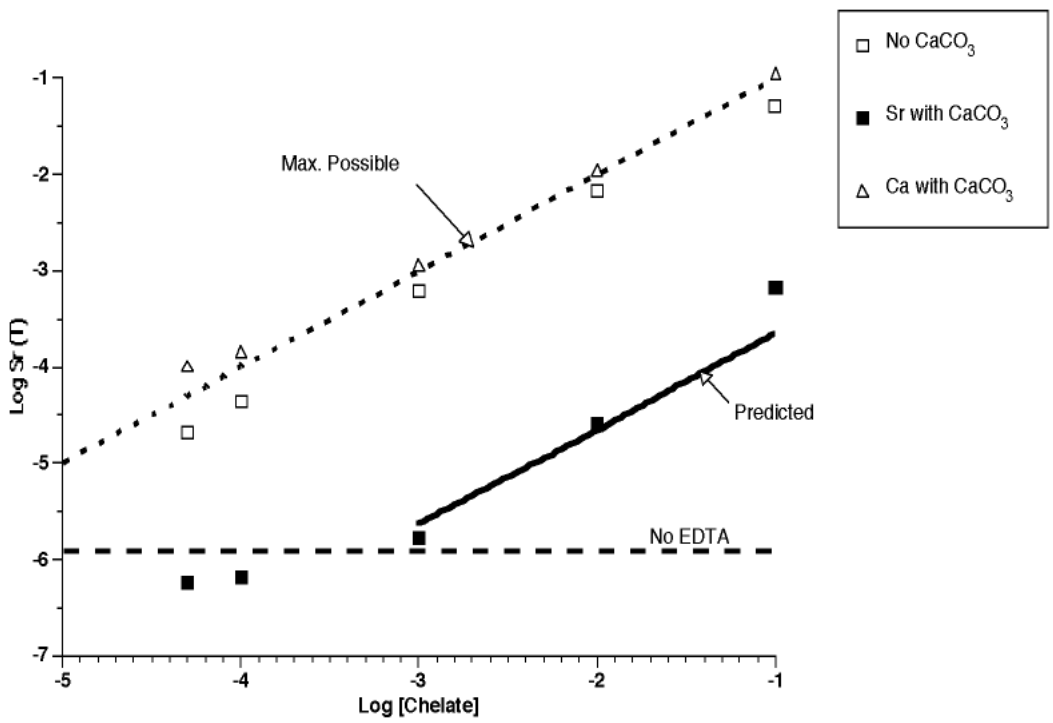


Figure 1. The solubility of $SrCO_3$(c) with added $CaCO_3$(c) in 0.1m Na_2CO_3. Solid lines represent model predictions.

Trivalent Actinide Studies

Studies on the solubility of Eu (III), a trivalent actinide analog, compounds [i.e. $Eu(OH)_3$(c)] were then completed as a function of base concentration in the presence of four organic chelates: EDTA, HEDTA, NTA, and IDA. $Eu(OH)_3$(c) was chosen for study owing to its very low solubility under high base concentration. These studies have shown that high base concentration can displace Eu(III) from all of the organic chelates studied. The effective NaOH concentration for the displacement reaction being dependent on the nature of the specific chelate studied and the chelate concentration.

Thermodynamic analysis of these experimental data, coupled with Time Resolved Laser Luminescence Spectroscopy (TRLFS) studies of the species in solution, indicated that formation of mixed metal-chelate-hydroxide complexes is occurring in solution. These mixed metal-chelate-hydroxide complexes increase the effectiveness of the chelates in solubilizing Eu(III) under high base conditions. The number of hydroxide ions bound to the metal-ligand complex varies with the chelate type. The structural and energetic reasons for this variability in solution corelate with density functional theory (DFT) calculations for gas phase La(III) clusters. In the case of EDTA and HEDTA, solution complexes form with either one or two hydroxyl ions associated with the metal-chelate complex (i.e. $Eu(OH)EDTA^{2-}$, $Eu(OH)HEDTA^{-}$, and $Eu(OH)_2HEDTA^{2-}$) whereas in the case of NTA

there is at most only one hydroxyl associated with the metal-chelate complex (e.g. $EuOHNTA^-$ or $EuOH(NTA)_2^{4-}$). The first determination of the stability constants for three of these species ($Eu(OH)EDTA^{2-}$, $Eu(OH)_2HEDTA^{2-}$, and $EuOH(NTA)_2^{4-}$) as well as for the $Eu(OH)_4^-$ species were determined. An aqueous thermodynamic model is presented which describes all of the available thermodynamic data for these chemical systems, to high ionic strength, and correlates with the DFT calculations.

The effects of these mixed metal-chelate-hydroxyl complexes is illustrated in Figure 2 for the solubility of Eu(OH)3(c) in EDTA solutions with added base. The formation of the mixed Eu-EDTA-OH complexes (specifically $EuOHEDTA^{2-}$) increases the solubility by orders of magnitude over the results in the absence of EDTA. Interestingly, the currently available thermodynamic models, which only include a $EuEDTA^-$ species, underpredict the observed solubilities by two to three orders of magnitude depending upon the hydroxide concentration. Clearly, predicting the effects of such speciation reactions is critical to understanding the solubility and aqueous thermodynamics of the trivalent actinides in chelate containing solutions under basic conditions.

These results have been presented at society meetings (Felmy et al. 1999; Felmy and Mason 1998) and the manuscripts have been published (Felmy and Rai 1999) or in press (Felmy et al. 2000).

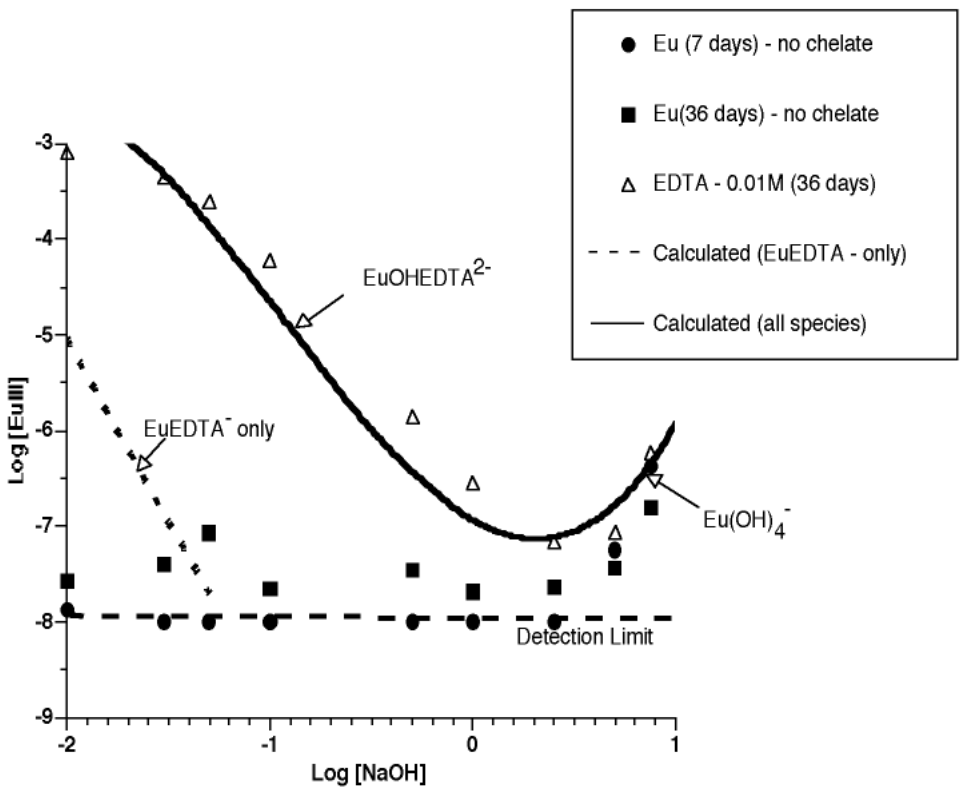


Figure 2. The solubility of $Eu(OH)_3(c)$ in NaOH in the presence and absence of 0.01m EDTA. Dashed line represents the model predictions before this study and without the $EuOHEDTA^{2-}$ species included. Solid line represents our current model predictions.

Implications for Waste Tank Processing

Sr Studies

These results have some interesting implications as regards processing basic/carbonate solutions such as those in high level tank waste. First, given the expected range in chelate concentrations present in tank waste and the fact that carbonate is present in significant concentration in all tanks, it is likely that the chemical speciation of Sr will be almost certainly unaffected by the presence of IDA

and probably also unaffected by the NTA as well. Only HEDTA and EDTA appear to be present at high enough concentration and form strong enough complexes to significantly impact the speciation of Sr in tank waste. Such results are important in limiting the number of chemical species that need to be considered in chemical modeling of tank processing strategies. In addition, competition with other metal ions present in such solutions, in this case Ca, can effectively displace Sr from the strong chelating agents HEDTA and EDTA, depending upon the concentration of Sr and the competing metal ions. This result indicates that metal ion displacement may represent an acceptable alternative to costly and hazardous organic destruction technologies in reducing the impacts of organic chelates in tank processing, especially given the fact that the chelators represent only a small fraction of the total organic carbon in tank waste. In a more general sense, these results also have direct implications to chemical processing applications under high base conditions where the build up of scale forming minerals (e.g. $CaCO_3$), can effect the removal of other metal ions by organic chelators.

Trivalent Actinides

The presence of the mixed metal-chelate-hydroxyl species can significantly impact waste tank processing strategies designed to either keep the trivalent actinides in the waste sludges or separate the actinides from the tank supernate. The solubility data themselves reveal that at chelate concentrations typical of tank solutions (i.e. ~0.01M) that basic solutions of 5M NaOH are required to remove the trivalent actinides from solution. This contrasts sharply with current model predictions that indicate that such removal should occur closer to 0.1M NaOH. The thermodynamic data developed here can be used in a wide range of applications including: evaluating the effects of competing metal ions on ligand displacement and solubility, evaluating the effects of waste mixing strategies from tank to tank, and determining the chemical forms and stability of complexes that can effect separation processes such as solvent extraction or ion exchange. Thermodynamic models capable of using these results are currently being used at Hanford and other sites. Finally, it should be noted that a significant fraction of the organic carbon present in tank waste (23-61%) is comprised of low molecular weight organic acids, such as acetate, glycolate, and formate. The results of this study for IDA indicate that even relatively strong ligands (Log K ~7) will not be able to solubilize trivalent actinides under basic conditions. Therefore, since most of the low molecular weight organic acids have relatively low binding constants with the trivalent actinides (Log K ~2-3) these ligands will probably not have much effect on tank processing strategies. Accurate thermodynamic models for these species are therefore not required.

In addition, the thermodynamic models developed as part of this study are currently being used by the Hanford private contractor (BNFL) to design better waste separation processes for Sr and the trivalent actinides.

Additional Research Needs

In order to extend these results to a wider range of waste tank compositions requires additional research in three areas: 1) extension to important chelates not previously studied, 2) studies of competing metal ions, and 3) specific studies using Am(III)/Cm(III). The chelate complex studies are needed to extend our previous research on EDTA, HEDTA, NTA, and IDA to citrate and oxalate. Mixed ligand-ligand complexation effects should also be addressed for Eu(III) in EDTA-HEDTA, EDTA-NTA, and HEDTA-NTA solutions to high base concentration. Studies of competing metals should include those metals (i.e Ni, Al, Mn, and Fe) which are present in highest concentration in the waste tanks. These fundamental data on chemical speciation and solubility will then be used to develop highly accurate thermodynamic models valid to high ionic strength. Such information will allow the analysis and modeling of a much wider range of tank waste compositions.

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Synthesis and Characterization of Templated Ion Exchange Resins for the Selective Complexation of Actinide Ions

Project ID: 59977

Dr. George M. Murray, Johns Hopkins University Applied Physics Lab

Dr. O. Manuel Uy, Johns Hopkins University Applied Physics Lab

Research Objective

The purpose of this research is to develop polymeric extractants for the selective complexation of uranyl ions (and subsequently other actinyl and actinide ions) from aqueous solutions. Selectivity for a specific actinide ion is obtained by providing the polymers with cavities lined with complexing ligands so arranged as to match the charge, coordination number, coordination geometry, and size of the actinide ion. These cavity-containing polymers are produced by using a specific actinide ion (or surrogate) as a template around which monomeric complexing ligands are polymerized. The polymers provide useful sequestering agents for removing actinide ions from wastes and will form the basis for a variety of analytical techniques for actinide determination.

Research Progress and Implications

This report summarizes the first thirty months of a three year project. During this period the majority of the polymers tested were synthesized using three coordinating ligand monomers: vinyl benzoic acid, vinyl salicylaldehyde and vinyl salicylaldoxime. Polymers have been applied to sequestration, ion selective electrodes and just recently the production of a selectively permeable membrane. A quantity of the above polymer composition has been applied to sequestration and preconcentration of uranyl from a complex matrix (seawater). The experiment was performed to see if the resin was capable of removing small amounts of uranium in a mixture of a wide variety of other metals ions, prior to determination by UV-VIS spectrophotometry. Several polymer formulations have been incorporated into membranes and tested as ion selective electrodes.

The formula used to make uranyl ion selective electrodes has been modified to extend the operational lifetime from weeks to months. The variables in the optimization of the electrode performance include: 1) adjusting polymer formulations, 2) varying the plasticizers and their relative amounts in the formulations, and 3) changing membrane compositions. The copolymers made with vinyl salicylaldoxime exhibit better selectivity than those prepared with vinyl benzoic acid. The calibration plots show that the response of the vinyl salicylaldoxime membranes to high levels of interfering ions is less than the response to uranyl ion at the detection limit. Attempts to make a composite membrane for the electrode has met limited success. The response of the composite membrane gave a lesser calibration slope and was erratic. The problems with the composite membrane stem from too great a thickness for conductivity.

Planned Activities

The uranyl ion sequestering agent will be optimized and tested against a broader range of interferences. Levels of crosslinking will be carefully evaluated in order to better understand the abrupt changes in selectivity. The ion selective electrode work will continue with the goal of fabricating membranes without using a PVC matrix. Plasticizer and ionophore will be added directly to the mixture of metal-ligand complex and spin-coated after the polymerization has been initiated in order to achieve

appropriate thicknesses. The selective ion permeating membrane will also be fabricated by the spin coating method to effect a higher uranyl throughput. The luminescent uranyl compounds will be used to construct optical sensors.

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Developing a Fundamental Basis for the Characterization, Separation, and Disposal of Plutonium and Other Actinides in High Level Radioactive Waste: The Effect of Temperature and Electrolyte Concentrations on Actinide Speciation

Project ID: 65352

Dr. Sue B. Clark, Washington State University

Dr. Linfeng Rao, Lawrence Berkeley National Laboratory
Dr. Scott Wood, University of Idaho

Research Objectives

This research involves establishing a foundation for describing the speciation of Pu and the other actinides in the extremely non-ideal systems found in HLW. We are developing a thermodynamic database of Pu and actinide complexing in alkaline systems, and at elevated temperatures and electrolyte concentrations. Initially, we are using chemical analogs for Pu; later we will conduct experiments using Pu itself. We are investigating complexation by OH^-, acetate, oxalate, and ethylenediaminetetraacetate ($EDTA^{4-}$). In addition, we are complementing our thermodynamic measurements with spectroscopic studies to validate assumptions made concerning speciation and stoichiometry.

Research Progress and Implications

This project began early in the 1999 fiscal year, and we have completed less than one year of the three year project. Our research progress and spending is on schedule. Initial work has been focused on the trivalent actinide systems, as models for Pu^{3+} and Am^{3+}. Prof. Wood's group at University of Idaho has been studying the solubility of the $Nd(OH)_3$ system as a function of temperature from 30-290°C. Their data are shown in Figure 1 (below).

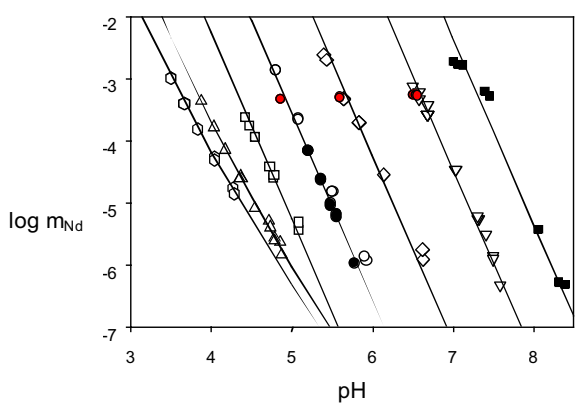

Figure 1: Plot of results of $Nd(OH)_3$ solubility experiments in 0.03 molal Na-triflate media as a function of pH at various temperatures. The temperatures of the data are, from right to left, 30°C, 50°C, 100°C, 150°C, 200°C, 250°C and 290°C. The symbols are the raw experimental data and the lines are best fits. The red symbols are replicate runs.

The dominant solubility controlling reaction in this system appears to be:

$$Nd(OH)_3(s) + 3H^+ \leftrightarrow Nd^{3+} + 3H_2O$$

Modeling of the reactions in the temperature range of 30-200° C indicates hydrolysis behavior is as expected. However, when T = 250 - 290° C, the data suggests *that $NdOH^{2+}$ is an important species, which is not predicted based on previous studies*. From this work, the stability quotient for the formation of the 1:1 hydrolysis species has been estimated, which now makes it possible to determine stability constants for complexation with acetate, oxalate, $EDTA^{4-}$, and other inorganic ligands under more alkaline conditions.

At Lawrence Berkeley National Laboratory (LBNL), the research group of Dr. Linfeng Rao has been studying the complexation of the trivalent *f*-elements with simple carboxylate ligands. Dr. Rao has measured the formation constants between Nd^{3+} (an analog for trivalent actinides) and acetate using potentiometry. Dr. Rao's results are shown below in Figure 2, and summarized in Table 1 (next page). Dr. Rao's results are consistent with unpublished work by Profs. Wood and Clark. As expected, these data show that complexation increases with increasing temperature. The formation constants of the 1:1, 1:2, and 1:3 complexes increase, but interestingly the 1:3 complex appears to increase more dramatically than the other two. *Such a marked increase in the formation constant of the 1:3 complex was not anticipated.*

To corroborate the results of Dr. Rao, research in Prof. Clark's group to date had focused on spectroscopic studies of the trivalent – acetate system. Lanthanide luminescence spectroscopy is being used to study speciation of Eu^{3+} in acetate as temperature is increased from 10 - 70° C. *The $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} emission spectrum increases markedly with temperature*. This indicates an overall increase in complexation, as shown by Prof. Wood and Dr. Rao. In addition, we are using high resolution of the $^5D_0 \rightarrow {}^7F_0$ transition to directly observe changes in the distribution of Eu^{3+} between the 1:1, 1:2, and 1:3 acetate species as a function of temperature. Spectral deconvolution of this transition at 25° C is shown in Figure 3. The effect of temperature on this transition is shown in Figure 4. Consistent with the results of Dr. Rao, *we see significant increases in the contributions of the 1:2 and 1:3 complexes, which were not expected.*

Our results demonstrate the importance of understanding the influence of temperature on the speciation of the actinides. *Our results show that a simple van't Hoff extrapolations of data representing ambient conditions has limitations especially for the treatment of the higher order complexes, and*

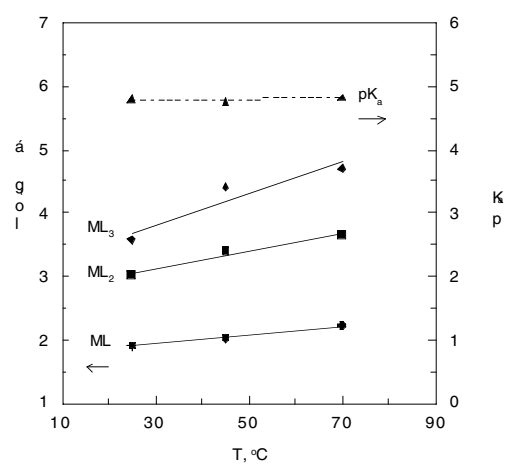

Figure 2: The constants of acetate protonation and complexation with Nd(III) at variable temperatures (Ionic strength = 2.0 M). The data at 25°C are from the literature (Smith and Martell, "Critical Stability Constants, Vol.6") for comparison.

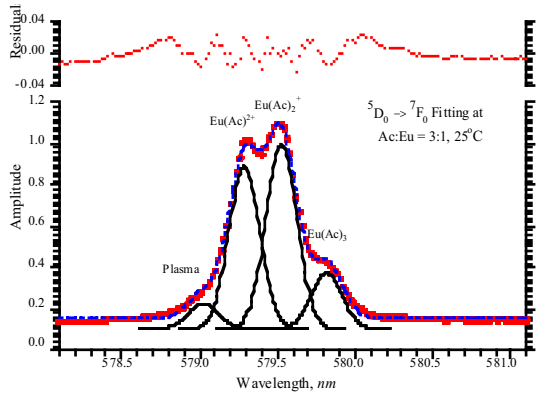

Figure 3: Spectral deconvolution of the $^5D_0 \rightarrow {}^7F_0$ transition of the Eu^{3+} emission spectrum. The 1:1, 1:2, and 1:3 species can be directly elucidated.

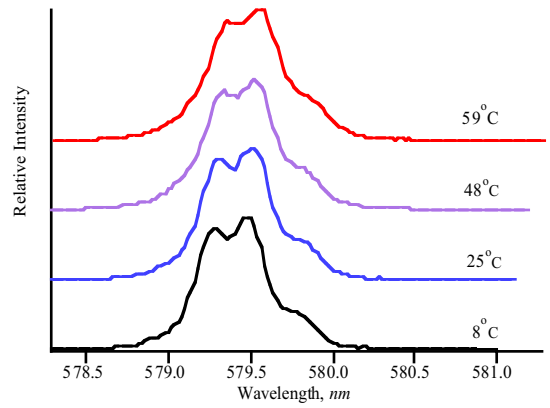

Figure 4: High resolution spectra of the $^5D_0 \rightarrow {}^7F_0$ transition of the Eu^{3+} emission spectrum as a function of temperature. Overall complexation increases markedly in this temperature range, and the prominence of the 1:2 and particularly the 1:3 peaks increase significantly.

Table 1 Thermodynamic parameters of acetate protonation and complexation with Nd(III) at different temperatures (Ionic strength = 2.0 M)

T, °C	log K[a]	log β_1[b]	log β_2[b]	log β_3[b]
25[c]	4.80 ± 0.01	1.92 ± 0.04	3.02 ± 0.05	3.58 ± 0.08
45	4.76 ± 0.01	2.05 ± 0.03	3.40 ± 0.05	4.36 ± 0.12
70	4.82 ± 0.01	2.24 ± 0.01	3.65 ± 0.03	4.71 ± 0.10

[a] $K = [HL]/([H^+][L^-])$, where L stands for acetate. The error limits from the data obtained in this work represent 3σ.

[b] $\beta_i = [ML_i]/([M][L]^i)$, where i = 1, 2 and 3, M and L stand for Nd and acetate. The error limits for the data obtained in this work represent 1σ.

[c] data at 25°C are from the literature (Smith and Martell, "Critical Stability Constants, Vol.6") for comparison.

that more experimental measurements are needed to extend existing thermodynamic models to consider elevated temperature systems. To date, we have made significant progress on the trivalent *f*-element system. Future work will focus on extending this work to include other actinides and Pu.

Planned Activities

For the next fiscal year, we plan to extend our complexation studies of the trivalent actinides into more alkaline pH regions. This is now possible based on the hydrolysis results of Prof. Wood. Prof. Wood's group will continue to study temperature regions in excess of 100° C. Prof. Clark's group will continue to pursue spectroscopic studies using other ligands (oxalate, $EDTA^{4-}$, nitrate, chloride, etc.). Dr. Rao is installing a calorimeter, which his group will use to directly measure enthalpies and entropies of reaction as a function of temperature.

We will also begin to study actinides in other oxidation states. Prof. Clark's research group is setting up potentiometric studies of the uranyl cation, and solvent extraction studies of the neptunyl cation. Prof. Wood's group is beginning to study the solubility of Th^{4+} in highly alkaline solutions; this work will aid in the planning of studies with Pu in various oxidation states.

Information Access

An extended summary was also submitted with this Progress Report.

"The aqueous geochemistry of the rare earth elements. IX. A potentiometric study of Nd^{3+} complexation with acetate in 0.1 molal NaCl solutions from 25-225° C, Geochim. Cosmochim. Acta, in press.

"A spectroscopic investigation of temperature effects on solution complexation in the Eu^{3+}-acetate system," M. Yeh, T. Riedener, K. Bray, and S. B. Clark, J. Alloys Compounds, submitted.

"Temperature dependence of chloride complexation for the trivalent *f*-elements", M. Yeh, A. Maddison, S. B. Clark, J. Radioanalyt. Nucl. Chem., submitted.