Decontamination/Decommissioning

Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation

Project ID: 60283

Michael Pellin, Argonne National Laboratory

Michael Savina, Argonne National Laboratory
Claude Reed, Argonne National Laboratory
Zhiyue Xu, Argonne National Laboratory
Yong Wang, Argonne National Laboratory

Research Objective

Laser ablation is being studied as a method both for removing and for measuring contaminated surface layers from concrete. The objectives of this research are to determine the mechanism and efficacy of laser ablation, to understand the chemistry of contaminated concrete surfaces, and to chemically and physically characterize the captured ablation effluent, which would become the stored waste. The method is attractive because it adds no additional waste, offers fine control over the amount of material removed, can work on cracked, curved or irregular surfaces, and can potentially be instrumented for real-time contamination analysis. While the focus of this project is on concrete, the technology should be applicable to any surface requiring contaminant removal.

Research Progress and Implications

This report summarizes work after 28 months of a three-year project. Concrete surfaces were ablated with an industrial pulsed Nd:YAG laser delivered via a fiber optic cable. The virgin and ablated surfaces and ablation effluent were chemically and physically characterized. In addition, optical emission spectra were obtained on-line during the laser ablation process itself.

We have shown that several different ablation mechanisms exist simultaneously when concrete is ablated at high power with a pulsed laser. The most important is the thermal shock created by the laser pulse. Rapid thermal expansion of a small volume of material causes stress to build up between the hot surface and cold bulk. When the thermally induced stress exceeds the tensile strength the material fractures into small pieces (up to a few millimeters in diameter) and explodes off the surface. This mechanism is particularly important in the aggregate portion of the concrete (i.e. sand and rocks) which typically makes up about 90% of the bulk of high density concrete, so that the overall material removal rate is dominated by this process. The ablation rate depends on several factors, most importantly laser power, but also pulse repetition rate, raster rate, focused spot diameter, and focal position with respect to the surface. In general, high power, fast raster rates and large beam diameters lead to the highest removal rates. The ablation efficiency, defined as mass removed per unit energy delivered to the surface, is unaffected by parameters such as total power or focused spot size. In particular, we have demonstrated that the ablation efficiency doesn't change over a wide range of irradiances (power per unit area). This is important for two reasons. First, concrete ablation with continuous wave lasers is critically sensitive to irradiance, and therefore more difficult to control and extrapolate from one laser system to another. Second, it shows that the pulsed laser process is scalable to lasers of arbitrary energy, since the laser spot size can always be easily adjusted to keep the irradiance within the wide bounds determined by this study. Hence the ablation rate scales only with the total laser power. This finding makes it possible to predict concrete ablation rates for any Nd:YAG laser system with pulse lengths similar to those used in our study, i.e. 0.5 to 1 ms.

We have found that efficiency drops at slow raster rates where consecutive pulses overlap significantly, leading to melting rather than ablation of the material. In this case the system behaves more like a continuous wave laser which glazes the surface as it passes over it. Excessive pulse overlap reduces the ablation efficiency in several ways. First, laser energy that would otherwise have been used to remove material is instead wasted in the energy-intensive phase transition required to melt the material. Second, the glazed surface is more reflective, resulting in reduced absorption of the laser energy in the overlapped region. Finally, residual heat left in the concrete from previous pulses reduces the thermal gradient induced by the overlapping pulse, thereby reducing the magnitude of the thermal shock.

The cement portion of the concrete comprises only about 10% of the total, but is important because it is the phase in which the bulk of the contamination resides in concrete that has been exposed to water-born radionuclide ions such as Cs and Sr. The cement phase can melt, spatter, vaporize, and/or disaggregate (i.e. explode) depending on the intensity and duration of the laser pulse. The laser-melted or -vaporized cement forms an aerosol that can have a very different chemical composition than the virgin cement. The aerosol particle size distribution is bimodal, with peaks at the high (8.5 μm) and low (<0.5 μm) ends and a minimum at about 1 μm. This suggests that particles form by two mechanisms, namely vaporization/condensation for small particles and melt/spatter for large particles. This interpretation is bolstered by energy dispersive x-ray spectroscopy, which showed that small particles had disproportionately large concentrations of aluminum compared to both the larger particles and the virgin cement. This suggests that small particles form by condensation from vapor, with an aluminum-rich nucleating phase. Neutron activation analysis (NAA) showed that cesium and strontium concentrations in the aerosol were also strongly correlated with particle size. Particles with aerodynamic diameters below 0.5 μm were enriched in cesium by up to a factor of two compared to the virgin cement, while larger particles were substantially depleted in cesium. In contrast, particles in the aerodynamic size range from 0.5 to 1.6 μm - the smallest of those formed by melt/spatter - were enriched in strontium by up to a factor of two over the virgin cement, while all others were depleted. The NAA data is consistent with the proposed particle formation mechanisms. Since cesium is very volatile compared to the other elements in the cement, it should be distilled out of the melted material and appear in the particles formed from the vapor phase. Strontium is less volatile and tends to remain with the melted/spattered fraction, though the reason for its preferential precipitation in the smaller of the melted particles is unclear.

Laser desorption mass spectrometry (LDMS) of cesium- and strontium-doped Portland cement and high density concrete samples showed that cesium resides in the adsorbed water in the cement pores, while strontium resided in the cement matrix itself. These results support the interpretation of the chemical fractionation observed in the ablation aerosol. LDMS analysis of ablated samples also demonstrated the potential for decontamination by laser ablation. A sample of the exterior surface of high density concrete exposed to an aqueous solution of CsCl was shown to have a 30- to 300-fold reduction of Cs after removal of 0.6 to 0.8 mm of material after a single high-power laser ablation pass.

Optical emission spectra of the ablation plume were collected and analyzed. A number of peaks were assigned to Cs and Sr, as well as many of the cement matrix elements. The high power and long pulse duration of the industrial Nd:YAG make it especially well suited to this type of analysis and offer the possibility of on-line analysis for a number of elements.

Planned Activities

Laser ablation studies will be extended to higher powers and the effect of varying pulse durations will be investigated. We will also compare the performance of Nd:YAG and CO_2 lasers to assess the effect of wavelength on the ablation efficiency and mechanisms. We will continue to investigate the use of laser-induced breakdown spectroscopy in this application as an on-line contaminant analysis tool.

Removal of Radioactive Cations and Anions from Polluted Water Using Ligand-Modified Colloid-Enhanced Ultrafiltration

Project ID: 60041

Dr. John F. Scamehorn, University of Oklahoma

Dr. Richard W. Taylor, University of Oklahoma
Dr. Cynthia E. Palmer, Lawrence Livermore National Laboratory

Research Objectives

The objectives of this project are to determine the feasibility of and develop optimum conditions for the use of colloid-enhanced ultrafiltration (CEUF) methods to remove and recover radionuclides and associated toxic non-radioactive contaminants from polluted water. The target metal ions are uranium, plutonium, thorium, strontium, cadmium, and lead along with chromium (as chromate). Anionic or amphiphilic chelating agents, used in conjunction with polyelectrolyte colloids, provide a means to confer selectivity required for removal of the target cations. This project entails a comprehensive study of the effects of solution composition and filtration unit operating parameters on the separation efficiency and selectivity of ligand modified colloid-enhanced ultrafiltration (LM-CEUF) processes. Problem areas identified by the Office of Environmental Management addressed by this project include removal of hazardous ionic materials from ground water, mixed waste, and aqueous waste solutions produced during decontamination and decommissioning operations. Separation and concentration of the target ions will result in a substantial reduction in the volume of material requiring disposal or long-term storage.

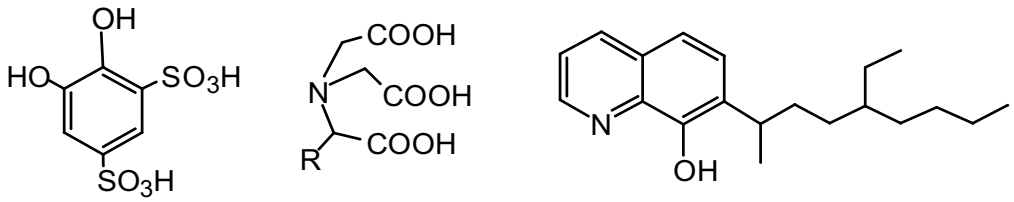
Research Progress and Implications

This report summarizes work after 2 years and 4 months of a 3-year project. In the method under study a soluble cationic colloid and an anionic or amphiphilic ligand are added to the waste stream to be treated. The ligands are attached to the colloid via electrostatic or hydrophobic interactions. The resulting feed solution is placed in a cell with an ultrafiltration (UF) membrane having pore sizes sufficiently small to reject the colloid along with any colloid-bound species. Target cations that form complexes with the ligands are retained during the filtration step. The degree of retention of the target ion X is expressed as a rejection coefficient, R_X (%), where $[X]_{per}$ and $[X]_{ret}$ refer to the concentrations of target species, X, in the permeate

$$R_X (\%) = \{ 1 - [X]_{per} / [X]_{ret} \} \times 100\% \quad (1)$$

(filtrate) and retentate (retained) solutions, respectively. Separation behavior was evaluated for the following metal ion-ligand systems: UO_2^{2+} with CO_3^{2-} and 1,2-dihydroxy-3,5-benzenedisulfonic acid, DHBSA (I); Th^{4+} with DHBSA; Pb^{2+} with nitrilotriacetic acid derivatives (II, RNTA); and Cd^{2+} with undecyl-8-hydroxyquinoline (III, $C_{11}HQ$). The ligand structures are shown below.

Ultrafiltration studies; separation and regeneration. For each system the effects of metal ion and ligand concentration, pH, added salt (NaCl), and colloid concentration were investigated. For electrostatic attachment of ligands, polydiallyldimethylammonium chloride (PDADMAC) was used as the colloid. Micellar-based separations employed the cationic surfactant cetyl pyridinium nitrate (CPN) or the neutral surfactant hexaoxyethylene-*n*-dodecyl ether ($C_{12}(EO)_6$. For the UO_2^{2+}-CO_3^{2-}



I DHBSA **II** RNTA **III** C11HQ

system at pH 7-8, R_{UO2} • 99.9% when the $[CO_3]:[UO_2]_{total}$ ratio is greater than 4.0. This result corresponds to UO_2^{2+} permeate concentrations as low as 0.1 micromolar, a reduction of about ~1000-fold in a single separation step. In the presence of 0.2 M or 0.5 M NaCl the R_{UO2} values decreased to ~95% and ~80%, respectively. Uranyl rejection decreased further, to ~70%, when the feed solution is adjusted to pH 2.4. The combined effects of lowered pH and increased salt concentration provide a potential method to remove UO_2^{2+} and recycle the polymer. DHBSA (I) was evaluated as a ligand for UO_2^{2+} and for Th^{4+}. With both metal ions rejection exceeded 99.9% in the pH range 5.0-6.5 for ligand:metal ratios equal to or greater than 2.0. The presence of 0.2 M NaCl caused R_{UO2} and R_{Th} to decrease slightly to 99.8% and 99.5%, respectively. Acid stripping (pH 1-2) gave ligand recoveries of about 50%. NTA derivatives (II) with anionic (R = $CH_2SO_3^-$, SNTA) and hydrophobic (R = $C_{10}H_{21}$, DNTA) substituents were tested for removal of Pb^{2+}. The latter was studied using CPN surfactant micelles as the colloidal phase. At low ionic strength SNTA gave R_{Pb} values in the range 99.0-99.9% while DNTA gave R_{Pb} values in the range 99.7-99.9%. In the presence of 0.05 M salt, R_{Pb} decreased to 50-55% for SNTA with PDADMAC, but was hardly affected (R_{Pb} = 99.5%) for DNTA with CPN. Acid stripping, combined with Pb^{2+} precipitation using oxalate, allowed ligand recoveries of 96% and 85% for SNTA and DNTA, respectively. An 8-hydroxyquinoline derivative, $C_{11}HQ$ (III) was tested for removal of Cd^2 using CPN and $C_{12}(EO)_6$ surfactant micelles as the colloidal phase. For both types of surfactant, R_{Cd} values in the range 99.0-99.7% were obtained at pH 9. The presence of added salt (10 mM NaCl) had no effect on rejection, R_{Cd} = 99.5-99.6% in either surfactant. High Cd^{2+} rejections were maintained in the mixtures containing either Ca^{2+} (R_{Cd} = 99.7%) or Zn^{2+} (R_{Cd} = 98.8%). Lowering pH to 6.0 resulted in ligand recoveries of ~88% (CPN) and ~50% ($C_{12}(EO)_6$.

Additional studies. The UF behavior of a cyclic phenol (calixarene) tetrasulfonate anion with PDADMAC was evaluated. Rejection values were greater than 99.8%, even in the presence of 0.5 M NaCl, indicating that calixarene derivatives are promising ligands for LM-PEUF at high electrolyte concentrations. A macrobicyclic polyether cryptand was evaluated and found to form strong complexes with Sr^{2+} (log K_{SrL} ~8.0 in water) with excellent selectivity (K_{SrL}/K_{ML} > 200) for Sr^{2+} relative to other alkali and alkaline-earth cations. Decyl thiourea, $C_{10}H_{21}NHC(=S)NH_2$, was tested using CPN as the colloid. Preliminary studies showed excellent rejection of Hg^{2+} in acidic solution (R_{Hg} = 99.8 at pH 2).

Planned Activities

During the next year, we will continue ultrafiltration studies on the LM-CEUF systems for removal of UO_2^{2+}, Th^{4+}, and Pb^{2+}. Focus will be on the chemical (pH, salt concentration) and physical (applied pressure, membrane pore size) parameters that affect separation efficiency as well as ligand and polymer recovery. UF techniques will be used to evaluate membrane binding and metal ion separation behavior of new ligands for other target cations (Pu^{4+}, Cd^{2+}, Sr^{2+}). Separations of other actinides (e.g., Pu) using LM-CEUF will be studied by collaborators at LLNL. Following evaluation in single cation studies, ligands displaying suitable performance will be tested using mixtures containing other cations and anions (e.g., CrO_4^{2-}).

Improved Decontamination: Interfacial, Transport, and Chemical Properties of Aqueous Surfactant Cleaners

Project ID: 64912

Dr. David W. DePaoli, Oak Ridge National Laboratory

Dr. Robert M. Counce, University of Tennessee
Michael Z.-C. Hu, Oak Ridge National Laboratory

Research Objective

This investigation is focused on decontamination using environmentally benign aqueous solutions, specifically the removal of organics and associated radionuclide and heavy-metal contaminants by surfactants. Aqueous-based solutions promise several advantages for decontamination processes, including low hazard potential, low cost, and reduced secondary waste volume through solvent recycle, solvent degradation, and/or incineration.

The work aims at gaining an understanding of interfacial, transport, and chemical processes that govern the effectiveness of aqueous-based surfactant solutions for decontamination of surfaces. In addition, efficient means for separation of waste materials from aqueous-based cleaners will be investigated. It is intended that the understanding developed in this work will be applied to decontamination/decommissioning tasks by laboratory testing of samples from DOE contaminated sites, and that the tests will provide the basis for improved approaches for removal of organic contamination.

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: R. M. Counce represented this project at the EMSP/D&D Workshop at Savannah River on November 17-18, 1998. This was a valuable meeting, describing in detail the problems associated with decontamination/decommissioning activities, and discussing the relevance of the EMSP projects to these problems. Although interest in this work was expressed by end-users, no ties to specific applications have yet been made.

Technical progress: Technical progress has been made in two areas: surface decontamination involving oil removal using aqueous-based surfactant solutions, and separation of waste from process materials. The first area deals with cleaning of surfaces, while the second addresses the subsequent task of treating the resultant solutions to minimize waste volume.

Surface Decontamination – Bench-scale experiments were carried out to investigate the removal of oil from surfaces using aqueous surfactant solutions. The experiments employed anionic, cationic, and nonionic surfactants; the surfactants involved were SDS, CTAB, and Triton X-100, respectively. The studies involved measurements of detachment time of single oil droplets from stainless steel coupon surfaces with varied solution chemistry. These experiments were carried out in an apparatus capable of monitoring contact angle evolution, droplet shape, and detachment.

The following are highlights of the results obtained to date:

1) Droplet detachment time is significantly affected by pH, surfactant type, and surfactant concentration.

2) We have discovered a simple modification that drastically decreases droplet removal time (nearly two orders of magnitude faster detachment in SDS solutions). An invention disclosure on this approach is in preparation.
3) Similar trends were obtained with single-droplet bench experiments and tests conducted using prototypic commercial cleaning equipment.
4) The agreement between bench and pilot tests suggests that miniature single-droplet experiments can be used effectively in a manner similar to combinatorial chemistry for rapid optimization of cleaning strategies with minimal investment of time and equipment and with low waste production.

Separation of Waste from Process Materials – studies are underway using synthesized effluents from aqueous-based cleaning operations. Anionic, cationic, and nonionic surfactants were used – SDS, CTAB, and Triton X-100, respectively. Three surfactant concentrations have been studied: at sub-critical micelle levels, near the critical micelle point, and above the critical micelle point. Phase splitting involving agitated surfactant solution is more complicated than that with oil and water alone; typically, 3 phases result from the separation, an oil-rich phase, a water-rich phase, and a surfactant-modified phase. The goal of this part of the experimental program is to understand how to design separation systems and to better understand the nature of the recovered materials so that wastes are minimized and useful materials such as the surfactants may be reclaimed for reuse.

Planned Activities

Planned activities include the following: (1) fundamental studies, (2) connection to applications, and (3) applicability studies. The fundamental studies will extend our current work and will be conducted to improve our understanding of the underlying mechanisms controlling both oil removal and phase disengagement. A particular focus will be placed on evaluating the effectiveness and feasibility of the simple process modification mentioned above, and comparison with other developed means of improving contaminant removal. Coupled studies will be aimed at further understanding ways to improve phase separation and media reuse, particularly taking advantage of knowledge gained in improving cleaning. Efforts will be continued in parallel to communicate the goals and results of this project with end-users at DOE facilities to determine pertinent applications. It is our intent to perform bench testing with surfaces and contaminants characteristic of such applications to determine whether the understanding developed in this project can help to improve DOE decontamination efforts.

Information Access

No results have been published to date.

Supercritical Carbon Dioxide-Soluble Ligands for Extracting Actinide Metal Ions from Porous Solids

Project ID: 64965

Dr. Mark L. Dietz, Argonne National Laboratory

Dr. Richard E. Barrans, Jr., Argonne National Laboratory
Dr. Albert W. Herlinger, Loyola University Chicago
Dr. Joan F. Brennecke, University of Notre Dame

Research Objective

The objective of this project is to develop novel, substituted diphosphonic acid ligands that can be used for supercritical carbon dioxide extraction (SCDE) of actinide ions from solid wastes. Specifically, selected diphosphonic acids, which are known to form extremely stable complexes with actinides in aqueous and organic solution, are to be rendered carbon dioxide-soluble by the introduction of appropriate alkyl- or silicon-containing substituents. The metal complexation chemistry of these new ligands in SC-CO_2 will then be investigated and techniques for their use in actinide extraction from porous solids developed.

Research Progress and Implications

This report summarizes the work performed during the first 1.3 years of a 3-year program. Because our planned studies of metal complexation and the development of techniques for actinide removal from solids are dependent on the availability of suitable ligands, our efforts to date have focused primarily on the synthesis of selected alkyl- or silicon-containing diphosphonic acids. Our principal targets have been derivatives in which the silicon-containing groups either serve as the ester function or are attached to the anchor carbon of the diphosphonic acid. Because methylenediphosphonic acid (MDPA) is commercially available and because its esterification with simple alcohols to yield symmetrical diesters is well-established, our initial studies have focused on this ligand and its reactions with silyl alcohols.

Success has been achieved in the reaction of MDPA and its ethylene, propylene, and butylene analogs with 3-(trimethylsilyl)-1-propanol. Using a procedure similar to that previously employed for the synthesis of C-8 dialkylmethylenediphosphonic acids, this series of alkylenediphosphonic acids has been esterified in good yield (ca. 60%) to the symmetrically-substituted diesters. Vapor phase osmometric and cryoscopic studies of these compounds in toluene and 1-decanol, respectively, indicate that their aggregation properties closely parallel those of the dialkyl-substituted alkylenediphosphonic acids, specifically, the P,P′-bis(2-ethylhexyl) alkylenediphosphonic acids, H_2DEH[ADP]. Infrared spectroscopy and molecular mechanics methods have been employed to obtain information about the structures of the dimers of P,P′-di-[3-(trimethylsilyl)-1-propylene] methylenediphosphonic acid, H_2TMSP[MDP], and its propylene analog. Infrared spectroscopy has also been employed to provide qualitative information on the binding of various metal ions by H_2TMSP[MDP]. The metal complexation properties of this ligand have been found to be similar to those of di-(2-ethylhexyl)methylenediphosphonic acid, examined previously. Studies of the extraction of various cations (*e.g.*, Fe(III), Th (IV), Am(III)) by H_2TMSP[MDP] and its ethylene analog in conventional organic diluents (*e.g.*, o-xylene) indicate that the extraction behavior of the silyl-derivatized diphosphonic acids closely mimics that of conventional alkylenediphosphonic acids. Thus, derivatization has no adverse impact on the complexation or extraction properties of the diphosphonic acids.

Planned Activities

Because our initial studies of the silyl-derivatized diphosphonic acids indicate that these compounds may lack sufficient SC-CO_2 solubility for the anticipated application, for the remainder of the current fiscal year, the synthesis and characterization of additional alkyl- and silicon-based diphosphonic acid derivatives will be carried out. In addition, we will investigate the use of modifiers as a means of improving the compatibility of the silyl derivatives with SC-CO_2. We expect that shortly, conditions suitable for the solubilization of adequate concentrations of diphosphonic acids in SC-CO_2 will be identified. Work to examine their metal complexation chemistry in SC-CO_2 will then be performed, along with the design and testing of procedures for the removal of actinides from porous solids.

Micelle Formation and Surface Interactions in Supercritical CO_2 Fundamental Studies for the Extraction of Actinides from Contaminated Surfaces

Project ID: 64865

T. Mark McCleskey, Los Alamos National Laboratory

Eva R. Birnbaum, Los Alamos National Laboratory

Research Objective

We are examining the potential of water in CO_2 microemulsions as a new medium for the extraction of metal ions from contaminated surfaces with the ultimate goal of extracting actinides from heterogeneous waste to aid in decontamination and waste reduction.

Research Progress and Implications

This report summarizes $1^1/_2$ years of work on a 3 year program. We report here on using water in CO_2 microemulsions as a new medium for metal extraction from contaminated surfaces. The nano-droplets of water suspended in CO_2 take advantage of both the high solubility of metal ions in water and the high diffusivity of CO_2 to penetrate pores that might be inaccessible to bulk water. The pressure-dependent solvent strength of CO_2 can be used to control formation of the nano-droplets. As the CO_2 pressure is dropped, a cloud point is reached where the nano-droplets coalesce into a water phase that is no longer suspended in the CO_2, allowing easy separation of the metal solution. This extraction scheme is particularly attractive for remediation of heterogeneous waste in which small amounts of metal contaminants are dispersed throughout a large volume of solid waste. Typically, such extractions require an amount of water or solvent proportional to the volume of solid material. With microemulsions, CO_2 is effectively used as a diluent and the amount of water need only be proportional to the amount of metal to be extracted, making it possible to decontaminate grams of waste with μL of water.

Extractions from Filter Paper - Extractions of copper from spiked filter paper were conducted to examine the effectiveness of the microemulsion in removing metal contaminates from solid surfaces. Greater than 99% of the copper is extracted in one step from the smaller pieces of filter paper. Extraction efficiency decreases when a larger piece of filter paper is used, but following with a second extraction again improves the efficiency to 83-99%. The kinetics of extraction from a spiked filter paper were followed by UV-Vis spectroscopy. The absorption from copper reached a maximum after 60 minutes of exposure to the microemulsion, with no further increase after an additional 90 minutes. The kinetics of extraction with microemulsions are much faster than those observed recently with CO_2-soluble polymers that required many hours to days for extraction. In addition to improved kinetics, the microemulsions have improved efficiency compared to previous studies with CO_2-soluble chelating agents. In general, past extractions have required a tremendous excess of ligand to achieve reasonable metal extractions (greater than 1000 fold). By comparison, at the maximum solubility of copper, the molar ratio of surfactant to copper in the microemulsion is approximately 3.

Luminescence Results - Europium fluorescence lifetimes and emission spectra were examined to probe ion solvation in the water in CO_2 microemulsions. The relative heights of the europium emission bands at 593 and 615 nm provide information on the first solvation sphere around the europium ion. When europium (III) is dissolved in water at ambient conditions, the ion is symmetrically hydrated by water and the transition at 615 nm is forbidden. In the microemulsion, the 615 nm band gains in

intensity, indicating that the center of inversion around europium is gone, due to displacement of water in the first hydration sphere by another ligand. Two possible ligands are available in the microemulsion core: the carboxylate head group of the surfactant or carbonic acid, formed by CO_2 dissolved in the aqueous phase. As a control, europium chloride was dissolved in D_2O and the headspace over the solution was pressurized to 3000 psi with carbon dioxide to introduce bicarbonate with no surfactant present. The europium emission spectra appeared the same as in water at ambient conditions, suggesting that the carboxylate head group of the surfactant is solely responsible for the changes in the emission spectra of europium ion dissolved in the microemulsion.

Further evidence for surfactant binding comes from lifetime experiments using H_2O- and D_2O-based microemulsions. The isotope effect provides a way to determine the number of water molecules surrounding the europium ion using the equation: $n = C^*(1/\tau_H - 1/\tau_D)$. The lifetime of europium (III) ion in the water in supercritical CO_2 microemulsion was found to be 120 µs and increased to 274 µs when the microemulsion was formed with D_2O. Using the above equation with the measured lifetimes gives approximately 5 water molecules in the first hydration sphere of the europium ions. As the fully hydrated ion has 8 to 9 water molecules, this result suggests that the surfactant displaces of 3 or 4 water molecules from around the europium ion.

Extraction of Metal Oxides - Radioactive and heavy metal contaminants are often present as water-insoluble metal oxides in heterogeneous waste. To demonstrate the versatility of the microemulsion in metal extraction, the microemulsion was formed with a 20 wt% nitric acid solution instead of pure water. The increase in acidity was confirmed by dissolving methyl orange indicator in the microemulsion. The indicator appeared bright red when the microemulsion was formed with 20% nitric acid as opposed to orange when distilled water was used. The ability of the acidic microemulsions to extract metal oxides was examined with europium oxide. Based upon visual observation, ten mg of europium oxide completely dissolved into a microemulsion formed with 20 wt% nitric acid after stirring for one hour.

Conclusions

Water in supercritical carbon dioxide microemulsions are effective for extraction of metals from solids. At maximum solubility, a 3 molar solution of copper can be obtained within the microemulsion core. The nano-droplets offer the advantages of rapid and efficient extractions with a versatile environment. Making the microemulsion with 20 wt% nitric acid rather than pure water allowed europium oxide to be solubilized. Agents that oxidize low valent metal oxides or known, inexpensive, water-soluble chelating agents could also be introduced into the microemulsions to expand the types of metals that may be extracted and to provide selectivity in mixed metal extractions. This could greatly expand the potential of CO_2-based extractions by eliminating the need to develop novel fluorinated ligands for each new extraction. Metal is readily recovered by simply dropping the CO_2 pressure below the cloud point, causing the water to coalesce into a single droplet with all of the metal and some surfactant. We are currently exploring the possibility of recovering the surfactant by washing with CO_2 and by increasing the water concentration once the extraction is complete to the point at which the microemulsions are no longer stable. The ability of the microemulsion to concentrate the metal into a small volume of water makes it particularly attractive for extractions from contaminated solids that often have small amounts of metal dispersed over a large volume of solid waste.

Planned Activities

During the remainder of the project we plan to:

1) Examine aspects of the surfactant that affect micelle formation such as chain length and charge.
2) Determine if water-soluble chelating agents can be added to promote specific metal extractions.
3) Control the pH within the microemulsion by changing the surfactant head group.
4) Characterize and test a newly synthesized phosphate based surfactant.
5) Extend extractions to look at depleted uranium, including uranyl and UO_2.
6) Explore extractions from a variety of matrices including cement and wood.

Decontamination of Radionuclides from Concrete During and After Thermal Treatment

Project ID: 64896

Dr. Brian P. Spalding, Oak Ridge National Laboratory

Dr. Zdenek P. Bazant, Northwestern University

Research Objective

This project will determine the effect of heating concrete on its engineering properties and the potential to remove common DOE radionuclide contaminants including ^{137}Cs, ^{90}Sr, ^{60}Co, and U. In the chemical properties subtask, effects on direct volatilization of radionuclides during heating, as well as their subsequent extractability behavior, will be established over a range of temperatures up to the melting point of Portland cement. The main objective of the mechanics and thermodynamics subtask of this investigation is to develop a powerful computational capability to evaluate the effects of various regimes of rapid heating of a contaminated concrete wall or slab.

Research Progress and Implications

This report summarizes research progress after 8 months (through June 1, 1999) of a 3-year project. In the laboratory studies of radioisotopic behavior, techniques for spiking Portland cement and following volatility of four radionuclides (^{134}Cs, ^{85}Sr, ^{57}Co, and natural U) have been completed. A sequential extraction procedure for Portland cement has been adapted to assay these radionuclides and their behavior in unheated cement determined as a baseline to compare responses after thermal treatments. A large uniform batch of hydrated (cured) Portland cement was prepared and pulverized to a narrow range of particle size (-100/+200 mesh) to provide a high-surface area/unit weight of cement and will facilitate following the volatile behavior of hundreds of radioisotopically-spiked cement samples and thousands of extractions of thermally perturbed cement samples. One gram samples of this pulverized cement, contained in 2-mL capacity refractory (alumina) crucibles, are spiked with the desired radioisotope and, after aging for several weeks, exposed to various temperatures and/or heating regimes. Retention of radioisotopes is assayed non-destructively, using gamma-ray spectroscopy of the crucibles, before and after thermal treatment. Preliminary results of the retention of these four radioisotopes by cement when heated up to 1400°C (cement melted) are presented in Figure 1 along with retention of moisture, calculated from the decreasing weight. Complete volatility of ^{134}Cs was observed at temperatures of 1200°C or greater. Thus, decontamination of ^{137}Cs from cement should prove quite feasible by direct heating. However, only minor volatility of the other radionuclides was observed so that their potential for decontamination will likely depend on their modified extraction behavior in thermally-perturbed cement.

The sequential extraction of the four radionuclides has only been completed for the thermally-unperturbed spiked cement samples (Figure 2). Both ^{134}Cs and ^{85}Sr were largely removed from cement in the first stages of the sequential extractions when only water was employed. This should be contrasted to their expected behavior if they had been incorporated into the cement during or prior to curing where they would be much less extractable because they would be incorporated within the hydrated silicate minerals rather than mostly adsorbed on surfaces. The highly alkaline nature of Portland cement, with its large excess $Ca(OH)_2$, probably caused the delay in extraction of both ^{57}Co and U until dilute hydrochloric acid was employed because these elements and radionuclides form highly insoluble hydroxides. Indeed, the release of both these radionuclides was delayed until the pH of the extracts decreased sharply, presumably after the excess $Ca(OH)_2$ had been neutralized by

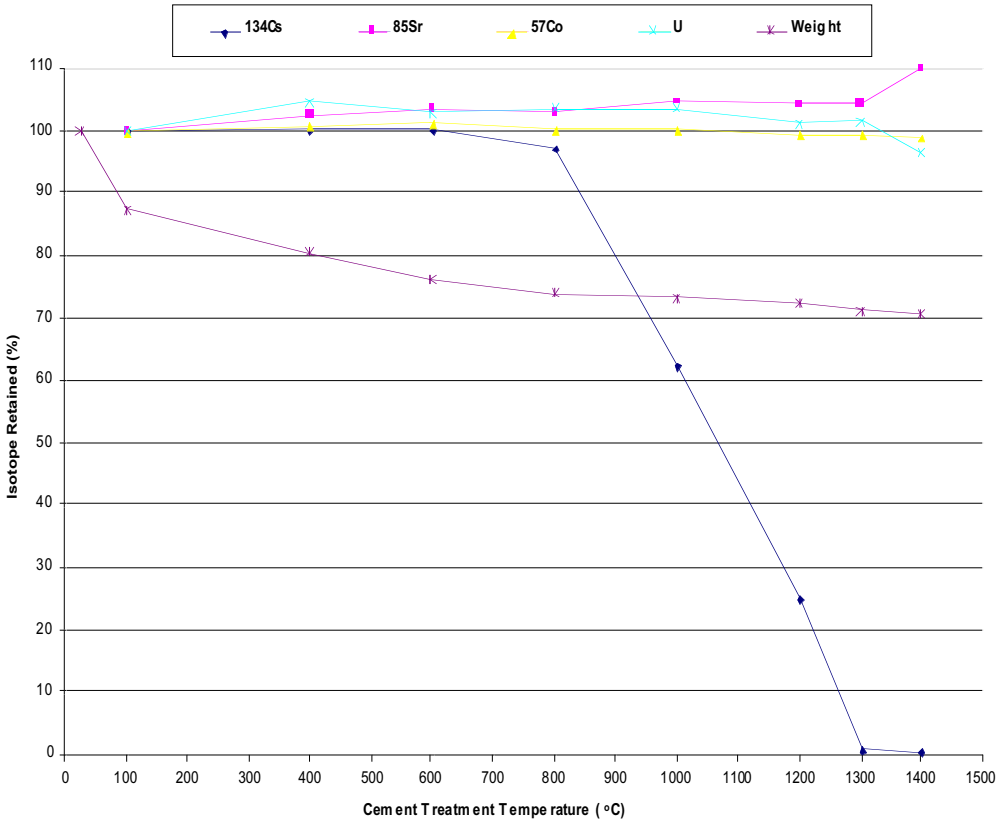


Figure 1. Retention of radionuclides by Portland cement after heating to various temperatures.

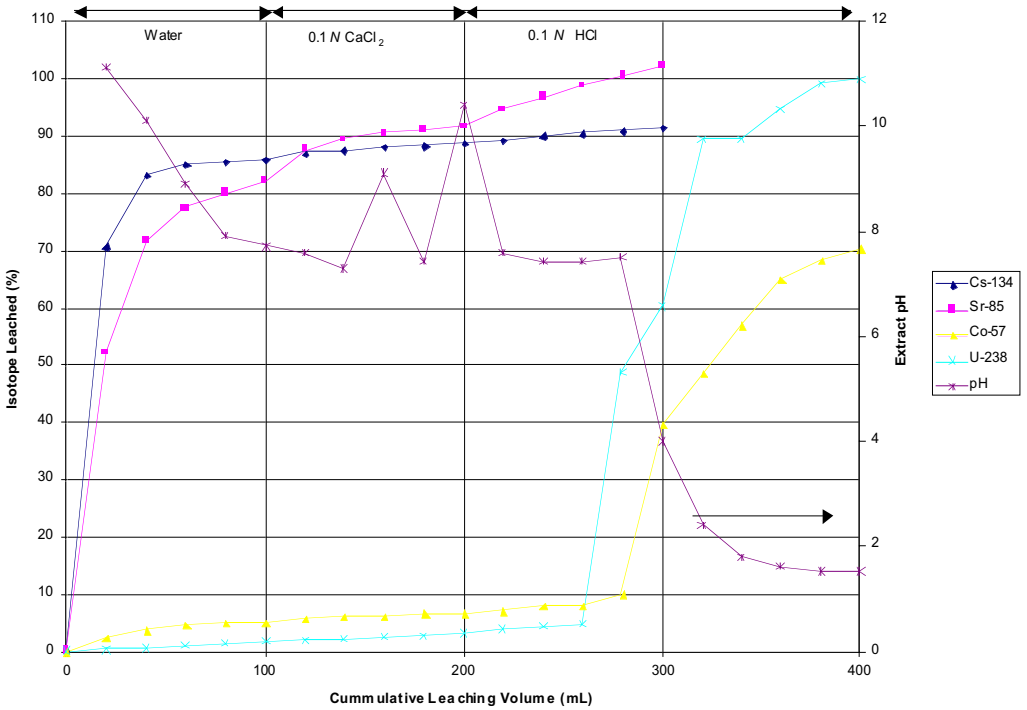


Figure 2. Sequential batch extraction of radioisotopes from Portland cement with water, dilute calcium chloride, and dilute hydrochloric acid.

the first five treatments with dilute HCl. At present, only this "baseline" of non-thermally altered cement extraction behavior has been completed. It is anticipated that significant changes in these extraction behaviors will be observed as cement is heated when significant mineral alterations are known to occur.

In the mechanics and thermodynamics subtask, the difficulty of modeling the heating of cement and concrete lies in the need to couple the heat and mass transport of pore water and various radionuclides it may contain. Previous studies in the field of nuclear reactor accidents used the finite element approach, which is plagued by instabilities at the sharp front of heating and propagating pressure. To overcome these difficulties, the finite volume method developed in the fields of geophysics and groundwater flow has been adopted and extended for the present coupled multiphase transport problem. By the time of this report a one-dimensional computer program has been developed, debugged, and successfully tested on example problems. The simulation of pore water is based directly on its known thermodynamic properties, with corrections for capillarity and adsorption. It is gratifying that the response converges well with volume refinements and is very stable.

At the same time, an alternative solution which has the potential of greater insight has been developed, utilizing the concept of moving layers with jumps in flux and pore water content at the interfaces. The velocity of the interfaces is obtained from Stefan type jump conditions. Analytical formulation of this second approach has been completed and numerical studies are starting.

Planned Activities

In the chemical subtask, the behavior of the four radionuclides, after themal treatment of cement, will be followed through the sequential extraction procedures. Heating rates and additions of volatility-enhancing chemicals will be tested on additional cement samples. Addition of aggregates, both siliceous and carbonate types, on the volatility and extraction behavior of these radionuclides will also be examined. Concomitant measurements of cement compressive strength will be obtained to correlate with the observed chemical changes mediated by thermal treatment.

In the modeling subtask, the two computational approaches will be tested by simulating the existing test data on rapid heating with pore pressure measurements. The next phase will deal with the calculation of thermal and hydraulic stresses caused by rapid heating, with a view to analyze fracture propagation and spalling.

Information Access

No publications from this project have yet been completed. Information on chemical extraction and radionuclide modeling for soil and for cement (coming soon) can be obtained at http://www.ornl.gov/LANGMUIR/bpsintro.htm.

"In-Situ" Spectro-Electrochemical Studies of Radionuclide-Contaminated Surface Films on Metals

Project ID: 55380

Carlos A. Melendres, Argonne National Laboratory

Susan Mini, Northern Illinois University
Azzam N. Mansour, Naval Surface Warfare Center

Executive Summary

The incorporation of heavy metal ions and radioactive contaminants into hydrous oxide films has been investigated in order to provide fundamental knowledge that could lead to the technological development of cost-effective processes and techniques for the decontamination of storage tanks, piping systems, surfaces, etc, in DOE nuclear facilities. The formation of oxide/hydroxide films was simulated by electrodeposition onto a graphite substrate from solutions of the appropriate metal salt. Synchrotron X-ray Absorption Spectroscopy (XAS), supplemented by Laser Raman Spectroscopy (LRS), was used to determine the structure and composition of the host oxide film, as well as the impurity ion. Results have been obtained for the incorporation of Ce, Sr, Cr, Fe, and U into hydrous nickel oxide films. Ce and Sr oxides/hydroxides are co-precipitated with the nickel oxides in separate phase domains. Cr and Fe, on the other hand, are able to substitute into Ni lattice sites or intercalate in the interlamellar positions of the brucite structure of $Ni(OH)_2$. U was found to co-deposit as a U(VI) hydroxide. The mode of incorporation of metal ions depends both on the size and charge of the metal ion. The structure of iron oxide (hydroxide) films prepared by both anodic and cathodic deposition has also been extensively studied. The structure of $Fe(OH)_2$ was determined to be similar to that of α-$Ni(OH)_2$. Anodic deposition from solutions containing Fe^{2+} results in a film with a structure similar to γ-FeOOH. From the knowledge gained from the present studies, principles and methods for decontamination have become apparent. Contaminants sorbed on oxide surfaces or co-precipitated may be removed by acid wash and selective dissolution or complexation. Ions incorporated into lattice sites and interlamellar layers will require more drastic cleaning procedures. Electropolishing and the use of an "electrochemical brush" are among concepts that should be considered seriously for the latter cases. The incorporation of radionuclides into the structure of highly defective, insoluble oxides and clays should be considered for long-term storage and disposal. The establishment of a truly long-term (10 to 20 years) basic program on environmental science by DOE is strongly recommended. Avenues for future work are suggested.

The application of the results obtained in this project to field problems was constantly kept in mind. It was facilitated by contacts with prospective users and attendance at conferences on decontamination and disposal problems. From the knowledge gained in this work, certain principles that would be useful in designing decontamination procedures are immediately apparent. Thus, it is evident that incorporation by lattice substitution into vacancies and in interlamellar positions is not likely to be common, especially for large metal ions, e.g. Sr^{2+}, U^{6+} ,etc. More facile and selective decontamination procedures such as acid washing and selective solvent dissolution by complexation could therefore be developed. Smaller metal ions which fit easily into vacancies in the defective structure of the host oxide or intercalate in the interlamellar structure would be more difficult to remove and thus require more drastic procedures. These ions may require hot acid washing, electropolishing, etc, to remove the whole surface coating. The use of electrochemical methods for radioactive decontamination is particularly interesting (private communications with R.P. Allen, Pacific Northwest National Laboratory, and D.B. Chamberlain, Argonne National Laboratory, 1996). Electropolishing has been demonstrated (R.P. Allen and H.W. Arrowsmith, Materials Performance

18, 216 (1979)) and appears promising; there is, however, a need for a better scientific understanding of the techniques that people have employed. Future work should address this issue. The novel concept of an "electrochemical brush" and other avenues for future work are discussed under the headings of "Productivity" and "Patents."

Finally, it is worthwhile to mention the relevance of the results obtained in this project to other areas of energy technology. Knowledge of the structure of metal ions incorporated into hydrous nickel oxides is of great importance in the further development of advanced nickel-based batteries, ultracapacitors, and electrochromic devices. Similarly, an understanding of the structure of iron and chromium oxides/hydroxides is vital to the development of corrosion inhibitors and the general problem of corrosion prevention.

Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic Surfaces

Project ID: 64946

Dr. A. J. Francis, Brookhaven National Laboratory

Research Objective

This project addresses key fundamental issues involved in the use of simple and safe methods for the removal of radioactive contamination from equipment and facilities using hydroxycarboxylic acids. The objectives of this research are to (i) determine the nature of the association of radionuclides with the metal surfaces commonly found at sites targeted for decontamination and decommissioning, such as plain carbon steel and stainless steel; (ii) selectively remove the low levels of radionuclides such as U, Pu, Co, Cs, and Sr from contaminated metallic surfaces using hydroxycarboxylic acids (citric acid and its analogs) by elucidating the coordination, complexation, dissolution and removal mechanisms; and (iii) recover radionuclides in a concentrated form by photochemical and biochemical degradation of the extract containing radionuclide-organic complexes thereby resulting in significant reduction in secondary waste generation. The basic information derived from this study should also be applicable to decontamination of other metallic surfaces as well as porous materials such as cement.

Research Progress and Implications

This report summarizes work after 17 months of a 3-year project. During this period we (i) synthesized the iron oxides ferrihydrite, goethite, green rust II, lepidocrocite, and magnetite containing U; (ii) determined the chemical composition and the nature of association of U with the oxides (total metal, XRD, XPS, FTIR, XANES, EXAFS); (iii) determined the dissolution profile of Fe and U from the oxides by i) HCl, and ii) citric acid; (iv) determined the rate and extent of biodegradation of citric acid in the extracts to remove citric acid; followed by photodegradation of the extracts to recover U; and (v) initiated studies with pre-, and post-rusted U contaminated plain carbon steel coupons to determine the nature of U association with the rust and the extent of decontamination with citric acid treatment. In addition, we collected ^{137}Cs and ^{60}Co contaminated rusts samples and characterized them for total activity and mineral phases.

Characterization of Iron Oxides Containing Uranium. Ferrihydrite ($Fe_2O_3 \cdot H_2O$), goethite (α-FeOOH), lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4), and green rust II with and without U, were analyzed for metal content; XRD for mineral form; XPS and FTIR to determine structural changes in the oxides as a result of U incorporation; and EXAFS to determine nearest neighbor association of U. These samples represent compounds typical of corrosion products formed on low carbon steel under atmospheric conditions.

The iron content of the oxides varied from 48 to 72%. Essentially all of the added U was incorporated in the oxide. The identification of the oxides with and without U was confirmed by comparing the X-ray diffraction patterns with the JCPDS library. Uranium containing samples showed additional spectral peaks indicating the presence of uranyl hydroxide with goethite, and uranium oxide or oxy-hydroxide with lepidocrocite and magnetite. EXAFS analysis at the U L_{III} edge showed the uranium near-neighbor environment is different for each oxide. A U-U interaction was observed at 3.8Å for magnetite and goethite, while U-Fe pairings were observed at 3.4 Å for ferrihydrite and lepidocrocite.

X-ray photoelectron spectroscopy analysis of the oxides containing U showed little change in the bulk material compared to the oxide without U, though slight reduction in the ionicity of the Fe-

oxyhydroxide bonding on the sample surface as a result of U adsorption is noted. FTIR spectra indicate adsorbed U appears to form a uranyl-hydroxo complex.

Decorporation of Uranium From the Oxides by Citric Acid. We determined the exchangeable form of Fe and U; the chemical association of U with the oxide by HCl dissolution; and the decorporation of U from the oxide by citric acid. HCl dissolution of the oxides showed complete dissolution of the U within the first hour of exposure. Correlation of the rate and extent of Fe with U dissolution varied in the following order: ferrihydrite >lepidocrocite >magnetite >goethite. Citric acid extraction efficiency of U from the oxides varied with the mineral form of the oxide. Uranium from goethite and magnetite was completely extracted by citric acid, whereas with ferrihydrite and lepidocrocite it increased with decreasing pH Complete dissolution of Fe from lepidocrocite and magnetite occurred at pH 3.5 but not at pH 2.2, indicating selectivity in the dissolution of these minerals by citric acid.

Corroded Steel Coupons. FTIR and XPS analyses were performed from the surface of low carbon steel coupons which were either dipped in a dilute uranyl nitrate solution or contaminated through atomization of a uranyl nitrate solution onto the coupon surface following various times of accelerated corrosion in a high humidity chamber developed for this program. All exposed samples showed a heterogeneous distribution of uranyl groups on the surface. Samples which were allowed to corrode further at 90% relative humidity for three days to one week following uranyl exposure showed some occlusion of the contaminant uranium by a loosely bound amorphous hydrated corrosion product. Surface areas covered by a thinner iron oxy-hydroxide corrosion layer showed stronger uranyl adsorption. The uranium-oxygen infrared stretching frequency was slightly shifted, indicating weaker bonding, whereas exposure to the acidic (uranyl) nitrate in solution resulted in an accelerated Fe corrosion product.

XPS data indicates that the uranium exists in a mixed U(VI)/U(IV) state following exposure to a lightly corroded or non-corroded surface and primarily as U(VI) when incorporated onto a heavily corroded steel surface. The samples were subsequently cleaned in a 0.1 M citric acid solution, and both the surfaces and the solution were analyzed. Citric acid was found to effectively chelate and remove uranium from all surfaces. Both FTIR and XPS analysis showed removal of most uranyl contamination by citric acid treatment. In addition, coupons exposed to citric acid were found to retain a thin layer of iron carboxylate which may act as a protective layer, thereby retarding additional atmospheric corrosion.

Secondary ion mass spectroscopy (SIMS) studies have been initiated on the contaminated and the rinsed surfaces. Data is currently being compared to the XPS and FTIR results.

Characterization of Contaminated Rust Samples. Rust samples collected from contaminated steels were analyzed for total activity, iron content, and mineral phases. The samples contained ^{137}Cs ($1.5x10^{-6}$ to $2.4x10^{-5}$ µCi/g) and/or ^{60}Co ($5.4x10^{-8}$ to $3.4x10^{-7}$ µCi/g). The iron content ranged from 54 to 80% in the samples. X-ray diffraction analysis showed the presence of magnetite, goethite, and/or lepidocrocite as predominant phases.

Planned Activities

- Characterization of radionuclides (U, Co, Cs and Sr) associated with plain carbon steel, stainless steel and copper pipes; elucidate the mechanisms of selective complexation and dissolution of the radionuclides by citric acid from contaminated steels (FY 2000).
- Decontamination of contaminated metallic surfaces obtained from DOE sites and treatment of waste stream by biodegradation followed by photodegradation with radionuclide recovery resulting in waste volume reduction and waste minimization (FY 2001).

Information Access

1. Halada, G.P., C.R. Clayton, M.J. Vasquez, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow, Interaction of Uranium with Corrosion Products Formed on Plain Carbon Steel. Paper presented at the 195th Meeting of the Electrochemical Society, May 2-6, 1999, Seattle, WA (Abstract. No. 108).

2. Halada, G.P., C.R. Clayton, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow. A Spectroscopic Study of the Association of Contaminant Uranium with Mild Steel Corrosion Products. Paper presented at the Symposium on First Accomplishments of Environmental Management Science Program, 218th American Chemical Society, Annual Meeting, August 22-26, 1999, New Orleans, LA, (paper NUCL-61).
3. Francis, A.J., C.J. Dodge, J.B. Gillow, G.P. Halada, and C.R. Clayton. Decontamination of Uranium Contaminated Metallic Surfaces with Uranium Recovery. Paper presented at the Symposium on First Accomplishments of Environmental Management Science Program, 218th American Chemical Society, Annual Meeting, August 22-26, 1999, New Orleans, LA, (paper NUCL-65).
4. Halada, G.P., C.R. Clayton, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow. A Study of the Interaction of Contaminant Uranium with Atmospheric Corrosion Products on Steel and Subsequent Complexation by Hydroxycarboxylic Acid, Paper presented at the 1999 Joint International Meeting, The Electrochemical Society and the Electrochemical Society of Japan, October 17-22, 1999, Honolulu, Hawaii (Abstract no. 617).
5. Halada, G.P., C.R. Clayton, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow. Removal of Contaminant Uranium from Corroded Steel Surfaces Using Citric Acid. Paper presented at the 1999 Tri-Service conference on Corrosion, organized by the U.S. Army Research laboratory Aberdeen proving Ground, MD Nov 15-19, 1999, Myrtle Beach, SC (Paper No.0006).
6. Halada, G.P., C.R. Clayton, A. Gupta, A.J. Francis, C.J. Dodge and J.B. Gillow. Removal of Contaminant Uranium from Corroded Steel Surfaces Using Citric Acid, Paper to be presented at the 197th Meeting of the Electrochemical Society, May 15-19 , 2000, Toronto, Canada

Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces

Project ID: 54914

Professor Robert F. Hicks, University of California

Dr. Gary S. Selwyn, Los Alamos National Laboratory

Research Objective

The purpose of this project is to develop a low-cost, environmentally benign technology for the decontamination and decommissioning of transuranic waste. In order to accomplish this goal, an understanding of the scientific principles of operating the atmospheric-pressure plasma jet must be achieved. This knowledge can then be applied to the design of a working tool for D & D applications within DOE.

Research Progress and Implications

Throughout the duration of this three-year project, this research has led to a fundamental understanding of high-pressure plasmas and their interaction with metal surfaces. We have characterized the plasma physics of an exciting new discharge that operates at atmospheric pressure. At the same time, we have identified the gas-phase chemical reactions occurring in oxygen-containing plasmas, and determined the surface kinetics of etching metals with plasmas. In addition to significantly advancing plasma and materials science, this research project should lead to new applications of plasmas in the ambient pressure regime.

We have demonstrated that by the addition of helium and by altering the electrode design, a plasma may be generated at atmospheric pressure that is weakly ionized with a neutral temperature of 75 to 125 °C. The electrons in this plasma are not in equilibrium with the rest of the gas: their energy is 2 to 3 electron volts, or more than 20,000 °C. The electrons are present in very low concentration. Nevertheless, they cause the dissociation of a significant fraction of the molecules present. For example, at an applied power of 24.4 Watts/cm^3 and 10 Torr O_2 in the feed, the plasma dissociates about 1% of the oxygen molecules into atoms (a concentration of ~10^{16} cm^{-3}). We found that by adding a few Torr of carbon tetrafluoride with the oxygen, the plasma generates a large flux of fluorine atoms. These fluorine atoms etch tantalum and other metals at several microns per minute. An examination of the surface chemistry has revealed that the etching rate is limited by the reaction of fluoride species with a metal fluoride layer on the tantalum substrate.

Planned Activities

Future work needed to implement this device for D&D applications include (a) identification of the reactive species in CF_4/He and CF_4/O_2/He plasma jets, (b) extension of the APPJ etching process to radioactive materials, (c) identification of volatile products and development of filtration techniques. Identification of the reactive species in the plasma jet is extremely important because we need this knowledge to increase metal etching efficiency, and to better understand how the volatile products are formed. It is also necessary to perform etching experiments with radioactive elements to determine tool effectiveness.

We have chosen to study the plasma etching of tantalum, because this element exhibits chemistry similar to plutonium and is a good surrogate material for the actinides. However, we expect there to be differences between the surface chemistry of etching tantalum and actinide metals, and these differences should be explored. Therefore, in the future, we propose to investigate the atmospheric-

pressure plasma etching of uranium oxide and metal films. We also propose to collaborate with scientists at Los Alamos National Laboratory to demonstrate the use of the plasma jet for an actual decontamination problem. An excellent test case would be to remove plutonium from the surfaces of glove boxes. This work would be carried out in the specialized facilities available at the Los Alamos laboratory.

Information Access

1. Jeong, J.Y., Babayan, S.E., Tu, V.J., Henins, I., Velarde, J., Selwyn, G.S. and Hicks, R.F., "Etching Materials with an Atmospheric-Pressure Plasma Jet," *Plasma Sources Sci. and Tech.* **7**, 282-285, 1998.
2. Schütze, A., Jeong, J.Y., Babayan, S.E., Park, J., Selwyn, G.S. and Hicks, R.F., "The Atmospheric-Pressure Plasma Jet: A Review and Comparison to other Plasma Sources," *IEEE Trans. Plasma Sci.* **26**, 1685-1694, 1998.
3. Jeong, J.Y., Babayan, S.E., Schütze, A., Tu, V.J., Park, J., Henins, I., Selwyn, G.S. and Hicks, R.F., "Etching polyimide with a non-equilibrium atmospheric-pressure plasma jet," *J. Vac. Sci. Technol. A* **17**, 2581-2585, 1999.
4. Park, J., Henins, I., Herrmann, H.W., Selwyn, G.S., Jeong, J.Y., Hicks, R.F., Shim, O., and Chang, C.S., "An Atmospheric Pressure Plasma Source," *Appl. Phys. Lett.*, **76**, 288-290 (2000).
5. J. Park, I. Henins, H.W. Herrmann and G.S. Selwyn, "Neutral Bremsstrahlung Measurement in Radio-Frequency (RF) Atmospheric-Pressure Discharge", submitted to *Phys. Rev. Lett.*, July 1, 1999.
6. Tu, V.J., Jeong, J.Y., Schütze, A., Babayan, S.E., Selwyn, G.S. and Hicks, R.F., "Tantalum Etching with a Non-Thermal Atmospheric-Pressure Plasma," submitted to *J. Vac. Sci. Technol. A*, February 11, 2000.

Optimization of Thermochemical, Kinetic, and Electrochemical Factors Governing Partitioning of Radionuclides during Melt Decontamination of Radioactively Contaminated Stainless Steel

Project ID: 60363

Dr. James A. Van Den Avyle, Sandia National Laboratories - Albuquerque

Dr. David Melgaard, Sandia National Laboratories
Dr. Martin Molecke, Sandia National Laboratories
Prof. Uday B. Pal, Boston University
Dr. Rodney L. Williamson, Sandia National Laboratories
Vasily V. Zhidkov, Mining and Chemical Combine

Research Objectives

The goal of this project is to characterize and optimize the use of molten slags to melt decontaminate radioactive stainless steel scrap metal. The major focus is on optimizing the electroslag remelting (ESR) process, a widely used industrial process for stainless steels and other alloys, which can produce high quality ingots directly suitable for forging, rolling, and parts fabrication. It is our goal to have a melting process ready for a DOE D&D demonstration at the end of the third year of EMSP sponsorship, and this technology could be applied to effective stainless steel scrap recycle for internal DOE applications. It also has potential international applications.

The technical approach has several elements: 1) characterize the thermodynamics and kinetics of slag/metal/contaminate reactions by models and experiments, 2) determine the capacity of slags for radioactive containment, 3) characterize the minimum levels of residual slags and contaminates in processed metal, and 4) create an experimental and model-based database on achievable levels of decontamination to support recycle applications. Much of the experimental work on this project is necessarily focussed on reactions of slags with surrogate compounds which behave similar to radioactive transuranic and actinide species.

This work is being conducted at three locations. At Boston University, Prof. Uday Pal's group conducts fundamental studies on electrochemical and thermochemical reactions among slags, metal, and surrogate contaminate compounds. The purpose of this work is to develop a detailed understanding of reactions in slags through small laboratory scale experiments and modeling. At Sandia, this fundamental information is applied to the design of electroslag melting experiments with surrogates to produce and characterize metal ingots. In addition, ESR furnace conditions are characterized, and both thermodynamic and ESR process models are utilized to optimize the process. To complete the process development, ESR melting experiments, which include actual radioactive contaminates as well as surrogates, are being conducted at the Mining & Chemical Combine in Zheleznogorsk, Russia. These experiments measure decontamination efficiencies in ingots for uranium and plutonium in stainless steel, as well as correlate removal of radioactive and surrogate compounds in the same melts. This will "close the loop" and allow us to use measured surrogate behaviors to model removal of radioactive species.

Research Progress and Implications

At Boston University, experiments were conducted to measure the dissolution of cerium oxide, as a surrogate for uranium and plutonium compounds, into the baseline ESR slag (60wt%CaF_2-20wt%CaO-

20wt%Al_2O_3). It was found that CeO_2 is very highly soluble into the slag, with the implication that the Ce concentration in the metal will be below the detection limit. This was experimentally seen in earlier ESR experiments. A volatilization study was conducted to determine the rate which the base slag with dissolved CeO_2 volatilizes as a function of temperature. The slag volatilization followed an Arrhenius behavior with temperature, and analyses of the volatile species showed them to be species generated from the base slag, with no ceria present. Physical property measurements on the molten baseline slag were performed. These data are needed for process characterization and modeling. These included slag viscosity, surface tension, and electrical conductivity from 1300 to 1700°C. Each of these properties showed Arrhenius behavior as a function of temperature.

At Sandia, several ESR experiments using nested pipe electrodes, which simulate scrap piping, were completed to determine the optimum furnace control strategy. This geometry of electrodes, made of reactor coolant piping, is used in the Russian furnace. Surrogate compounds and their concentrations were selected for the Sandia and Russian experiments. Surrogates include CeO_2, (to represent uranium and plutonium oxides), CsF, and SrO (non-radioactive forms of radioactive fission products), HfO2 (oxide with density similar to uranium oxide), and ReO_2 (surrogate for ^{99}Tc)

A series of six ESR experiments was begun to assess the influence of melt rate, slag composition, and slag additives. These melts used the surrogates listed above and were highly instrumented to measure slag temperatures, thermal performance, and furnace electrical characteristics. Chemical analysis of the slag samples and metal ingots is underway to determine chemical partitioning efficiency.

Thermodynamic modeling at Sandia using the commercial software MTDATA predicts that all surrogates should strongly partition to the slag, except for Re, which should end up in the metal phase. All Cs compounds should vaporize, and uranium compounds should not. Tc and Co would also go into the metal.

Under a Sandia project funded by another DOE program (IPP), two ESR melting experiments using plutonium contaminated pipe electrodes were run at the Mining & Chemical Combine in Russia. Analyses of ingot material and slag showed very effective partitioning of the Pu to the slag and decontamination of the metal. Under EMSP, we are funding two additional experiments this summer to determine slag reactions with plutonium and uranium oxides, as well as the surrogates. Results of these experiments will allow us to directly correlate the behaviors of radioactive species with their surrogates. This should validate our ability to predict decontamination efficiencies at different furnace operating conditions and allow us to optimize the process using surrogates.

Planned Activities

These are the planned activities during the final year of this EMSP project:

Boston University

1. Measure the dissolution kinetics of cerium oxide surrogate compound in the baseline slag (60% CaF, 20% Al2O3, 20% CaO) and measure the partitioning of cerium between the molten slag and molten metal in equilibrium at elevated temperatures.

2. Measure the electrical conductivity of baseline slag with additions of titanium oxide to 4, 8, and 12 wt. % and addition of cerium oxide to 4 wt. % (no titanium oxide).

3. Measure the solubility of hafnium oxide and strontium oxide at 100 to 5000 ppm initial quantity in baseline slag.

4. Measure baseline slag volatility with strontium oxide surrogate additive (5000 ppm).

5. Perform thermodynamic modeling of slag-metal (stainless steel)-surrogate/contaminate systems and coordinate with modeling activities at Sandia. Surrogate/contaminate species of interest include Ce, U, Pu, Cs, Sr, and Tc.

6. Measure slag physical properties including contact angle, surface tension, and viscosity of slags with surrogate additives .

Sandia:

1. Perform thermodynamic modeling of slag/surrogate/metal systems.
2. Complete ESR furnace experiments and analyses of chemical, temperature, and electrical data.
3. Analyze results of ESR melting experiments performed at M&CC in Russia and correlate with laboratory experiments with surrogates.
4. Define optimum ESR furnace design and operation to propose for D&D demonstration.

Mining & Chemical Combine:

1. Conduct two ESR furnace experiments using pipe electrodes contaminated with Pu, U, and surrogates. Two slag chemistries will be tested.
2. Analyze the stainless steel ingots at bottom, middle, and top to measure concentrations of contaminates, surrogates, and alloy content. Also analyze the slag skin and slag cap from each melting experiment.

Modeling of Diffusion of Plutonium in Other Metals and of Gaseous Species in Plutonium-Based Systems

Project ID: 59925

Bernard R. Cooper, West Virginia University

Gayanath W. Fernando, University of Connecticut

Research Objective

The problem being addressed is to establish standards for temperature conditions under which plutonium, uranium, or neptunium from nuclear wastes permeates steel, with which it is in contact, by diffusion processes. The primary focus is on plutonium because of the greater difficulties created by the peculiarities of face-centered-cubic-stabilized (delta) plutonium (the form used in the technology generating the waste).

Temperature is the key controllable diffusion processes, i.e., temperature controls the rate of diffusion. The scientific goal of this project is to predict diffusion constants on an ab initio basis, i.e. diffusion distances in specified time at specified temperature for plutonium from plutonium-based waste materials into various steels or technologically-pertinent metallic alloys. This predictive ability will help to provide information relevant to setting temperature standards for maintaining structures, ducts, equipment, or waste-containing vessels until such time as decontamination and decommissioning and/or permanent storage can be carried out. In addition, this knowledge will aid in assessing the depth of penetration that must be dealt with in any surface treatment for decontamination.

The scientific steps of the methodology are (1) to recognize the stabilizing mechanism and the electronic structure pertinent to that stabilization for face-centered-cubic (fcc) delta-stabilized plutonium, (2) to extract the information needed to perform dynamic simulations from ab initio electronic structure calculations, (3) to perform and report the dynamic simulations predicting the diffusion behavior.

Research Progress and Implications

This report summarizes progress after 2 1/2 years of a 3-year project. We have completed step (1) recognizing the stabilizing mechanism and the electronic structure pertinent to that stabilization for face-centered-cubic (fcc) delta-stabilized plutonium; and the substantial computations and modeling for (2) and (3) are in progress. The related experimental work is underway at Los Alamos National Laboratory, and the linkage between our work and that at LANL has been established in detail.

To model diffusion of the stabilizing element atoms, e.g., gallium, within delta (fcc) plutonium wastes and then into the steel of containers requires obtaining information about the electronic structure of fcc Pu in physically accurate yet tractable form. We are working on several aspects of developing that methodology and generating that necessary information. This work falls within a conceptual framework based on our understanding of the unusual structural behavior found in elemental plutonium. It has been evident for some time that this behavior is related to the localization mechanism for the 5*f* electrons in going from alpha to delta (fcc) plutonium. We explain this behavior on the basis of a multistep 5*f* localization process involving spatially nonuniform localization. That is, we suggest that a disordered array of two types of plutonium on crystallographically equivalent fcc sites breaks the translational symmetry and provides an entropy generating mechanism that drives these transitions. The two types of plutonium sites are: first the fluctuating para sites, at which the number of localized *f* electrons fluctuates between f^4 and f^5 because of hybridization with non-*f* band electrons, and second the localized ortho sites, at which the number of localized *f* electrons remain stable at f^5.

It is the entropy of mixing between these two types of sites that drives the thermal stepwise (via beta and gamma) transition from the monoclinic alpha ground state to the face-centered-cubic delta phase.

(1) We are implementing our theory that provides fundamental understanding of the phase stabilization of fcc Pu on the basis of a stepwise localization of the 5*f* electrons into a solid-solution-like phase, as described above. We have designed and are carrying out large-scale calculations that will reproduce the fully self-induced or stabilizer-nucleated Anderson (disorder) localization that leads to this phase. These calculations involve two-electron dynamics as opposed to the one-electron dynamics of LDA (local density approximation)-based methods.

(2) Until such time as the very large-scale calculations required in (1) are fully implemented, we are pursuing an immediately practical alternative for generating the data needed to model diffusion. We have developed variations of both the LDA+U and LDA-SIC (self-interaction-corrected) methods appropriate to *f*-state localization and applied these to fcc plutonium. These calculations give an atomic volume of fcc Pu about 6% smaller than the experimental value. Having the total energy from such a calculation together with that from a conventional LDA calculation for the monoclinic alpha ground state also enables us to predict the stabilization temperature of the delta (fcc) phase.

(3) We have recognized the importance of correctly treating the localization of the 6p as well as the 5*f* electronic states in fcc Pu, and thereby recognized the importance of specific relativistic effects for the 6p electrons. We are developing methodology to treat these effects.

Planned Activities

As stated above, we have developed a detailed technical plan for proceeding with steps (2, extracting the information needed to perform dynamic simulations from ab initio electronic structure calculations) and (3, performing and reporting the dynamic simulations predicting the diffusion behavior). We currently are proceeding systematically through the detailed parts of this plan.

Information Access

Publications

"The Role of Anderson Localization in Causing the fcc Stabilization and the Depressed Melting Temperature of Plutonium" B.R. Cooper, to appear in Los Alamos Science, 2000.

"A Theoretical Study of Relativistic Effects in the Electronic Structure of Pu", accepted to appear in Physical Review B (2000). (G.W. Fernando, E.H. Sevilla, and B.R. Cooper).

"Correlation Effects on Stability in Pu Metal and Its Alloys", pp 531-537 in Electron Correlations and Materials Properties (A. Gonis and N. Kioussis, Eds., Plenum Publishing, 1999) (B.R. Cooper with P.E.A. Turchi, A. Gonis, N. Kioussis, and D.L. Price).

"From Heavy Fermions to Random-Localized-Site Behavior Via Anderson Localization", Philosophical Magazine B 79, 683 (1999). (B.R. Cooper with O. Vogt, Q.G. Sheng, and Y.L. Lin).

"Calculated Lattice Relaxation in Pu-Ga Alloys", Journal of Alloys and Compounds 271-273, 367 (1998). (B.R. Cooper with J.D. Becker, J.M. Wills, and L. Cox).

"Calculated Lattice Relaxation in Pu-Ga", Phys. Rev. B 58B, 5143 (1998). (B.R. Cooper with J.D. Becker, J.M. Wills, and L. Cox).

Invited Talks at International Conferences

"From Heavy Fermions to Random-Localized-Site *f*-Electronic and Magnetic Behavior Via Anderson Localization", European Conference on Physics of Magnetism 99", Poznan, Poland, June 21-25, 1999.

"The Role of Exchange in Correlated-Electron Dynamics", Czech-US Workshop on Prospects of a Realistic Description of Strong Electron Correlations in Solids, Prague, October 1-6, 1999.

"Treating Electronic and Magnetic Properties of Actinide-Based Materials Beyond One-Electron Dynamics", School of Actinide Physics and Chemistry, Uppsala, Sweden, May, 1998.

"Synthesis of Many-Body Theory and Electronic Structure", International Workshop on Electron Correlations and Materials Properties, Heraklion, Crete, Greece, June 28-July 3, 1998.

Contributed Presentations at Conferences

"Structural Relaxation in Pu-Ga via Full-Potential LMTO Calculations", Actinides 97 International Conference, Baden-Baden, Germany, September, 1997. (B.R. Cooper with J.D. Becker, J.M. Wills, and L. Cox).

"Diffusion of Plutonium into Transition Metallic Alloys and of Transition Metal Species into Plutonium", Eighth Conference on Computational Research on Materials, Lakeview, WV, May, 1998. (B.R. Cooper with S. Beiden).

"Modeling of Diffusion of Plutonium in Other Metals and of Gaseous Species in Plutonium-Based Systems", Environmental Management Workshop, Chicago, July, 1998. (B.R. Cooper with S. Beiden).

"Portable Detection and Analysis of Plutonium Content", Workshop on Environmental Management Science: Integration with End User Needs, Savannah River Site, November, 1998. (B.R. Cooper with D. Leder).

"Modeling of Diffusion of Plutonium", Workshop on Environmental Management Science: Integration with End User Needs, Savannah River Site, November, 1998. (B.R. Cooper with S. Beiden).

"Modeling of Interdiffusion of Plutonium and Other Metals", Materials Research Society Meeting, Boston, November, 1998. (B.R. Cooper with S. Beiden).

"Anomalous Electronic Behavior and Relationship to Thermostructural Behavior of Light Actinides", American Physical Society Meeting, Atlanta, March, 1999.

"Electronic Structure of Alpha and Delta Plutonium", American Physical Society Meeting, Atlanta, March, 1999. (B.R. Cooper with N. Kioussis, P.E.A. Turchi, A. Gonis and D.L. Price).

"Equilibrium Lattice Volume of fcc Pu", American Physical Society Meeting, Atlanta, March, 1999. (B.R. Cooper with E.H. Sevilla and G.W. Fernando).

"Random 5*f* Localization and the fcc Transition and Depression of Melting Temperature in Plutonium, 29th Journees des Actinides Conference, Luso, Portugal, April 1999.

Synthesis of New Water-Soluble Metal-Binding Polymers: Combinatorial Chemistry Approach

Project ID: 54724

Dr. Barbara F. Smith, Los Alamos National Laboratory

Dr. R. Bryan Miller, University of California at Davis
Dr. Mark J. Kurth, University of California at Davis
Dr. Samuel Sawan, University of Massachusetts at Lowell

Research Objective

(1) Develop rapid discovery and optimization approaches to new water-soluble chelating polymers for use in Polymer Filtration (PF) systems and (2) evaluate the concept of using water and organic soluble polymers as new "solid" supports for combinatorial synthesis.

Research Progress and Implications

Polymer Filtration (PF), which uses water-soluble metal-binding polymers to sequester metal ions in dilute solution with ultrafiltration (UF) to separate the polymers, is a new technology to selectively remove or recover hazardous and valuable metal ions. Future directions in PF must include rapid development, testing, and characterization of new metal-binding polymers. Thus, we are building upon and adapting the combinatorial chemistry approach developed for rapid molecule generation for the drug industry to the rapid development of new chelating polymers.

We have focused on four areas including the development of: (1) synthetic procedures, (2) small ultrafiltration equipment compatible with organic-and aqueous-based combinatorial synthesis, (3) rapid assay techniques, and (4) polymer characterization techniques.

(1) Synthetic Methods Development: Several classes of materials are being developed: (1) acylpyrazolones, (2) polyisoxazoles, (3) 1,2-aminoalcohols, and (4) pendant-heteroatoms. Recently, we have focused our efforts at obtaining polymers rather than small molecules; and in this effort we have synthesized a wide variety of simple polyacrylamide-containing ligands in order to calibrate our efforts. The polyisoxazole syntheses utilize the 1,3-dipolar cycloaddition of nitrile oxides with alkynes as the dipolarophile. The hope is that these isoxazoles along with other electron donating atoms will have favorable metal binding properties. Our goal is to synthesize a 3,3'-diisoxazole and then tether it with other heterocycles to form tetradentate ligands. Our studies on the construction of pyrazoloisoxazol-(in)e-based heterocycle, utilizing the intramolecular cycloaddition of 1,3-dipole, in turn generated from dipolarophile "tethered" pyrazolo aldehyde have continued. In the acylpyrazolones, we have prepared over 40 derivatives having variation mainly in the side chain at C-4. A variety of heterocycles having multidentate ligands such as thiophene, furan, and pyridine have been prepared.

(2) Small Ultrafiltration Equipment: We have built a unit based on reverse dead-end ultrafiltration. This filtration is faster than a dead-end filter as we are not producing a gel concentration polarization layer on the membrane. We are using centrifugal force as the pressure source to drive the liquid through the membrane. Right now the unit material of construction is a polypropylene housing with a polysulfone membrane. The synthesis can be performed in separate glass or plastic tubes. At the end of the reaction the filtration unit is placed in the tube and then ultrafiltered, driving the solution into the filtration unit from the under side.

3) Rapid Polymer Assaying Techniques: *Micro-X-ray fluorescence (MXRMF):*: We have been able to optimize the spot drying technique, deal with background noise, optimize thickness and size of the spot, evaluate Mylar base materials, improve sensitivity, and do multi-element analysis. Better sensitivity is realized with lower polymer concentration. We have been successful in detecting 10 ppb concentrations of metal ions in an aqueous test solution. Further improvements with apertures on both the X-ray tube and the detector may increase the method sensitivity.

Radiochemistry: Tests using autoradiography proved to be too slow for a rapid survey approach. Thus we developed a rapid survey technique using direct counting techniques of the ultrafiltration units. We have adapted commercially available, centrifugation driven UF units developed for protein purification to a rapid survey technique of our polymers under various conditions. They use a dead-end filtration and have sample volumes from 0.5 to 2 mL. The membranes we use typically have a molecular weight cut off (MWCO) of 10,000 to 100,000 Daltons and are composed of a variety of membrane materials such as cellulose acetate, polysulfone, and fluoropolymers.

(4) Polymer Characterization: The weight average molecular weights, as well as other characteristics such as the second virial coefficients and root-mean-square (RMS) radii of gyration of polyamines and various derivatives, have been determined in solution light scattering studies. The solution dynamics of polyamines and carboxylated and phosphorylated derivatives were studied at pH 3.3, 7.0 and 10.0. Measurements were made in freshly distilled and de-ionized water as well as in 0.1 M, 1 M and 5-M solutions of sodium chloride in water. Molecular weights were calculated from Berry plots. The concentration of sodium chloride leads to an increase in the root mean square radius of gyration, as the polymer chains become more extended and relaxed in a more concentrated salt medium. The apparent molecular weights are observed to decrease in proceeding from acidic to alkaline medium, especially with the phosphorylated polymer. However, the RMS radius of gyration of the carboxyl modified polymer was high at both ends of the pH scale, i.e., the polymer chains were extended at both the acidic and alkaline pH ends. The increase in RMS radius of gyration is indicative of increasing solvent-polymer interaction.

Planned Activities

Overall activities will include completion of the synthetic methods development and preparing polymers for testing, performing the combinatorial synthesis, testing the polymers on a suite of metals, and characterizing the best candidates. The rapid assay techniques are almost complete, and the polymer characterization direction is towards Cd-NMR. A number of manuscripts are in progress.

Information Access

Patent disclosures have been filed to aid in technology transfer

B. F. Smith, T. W. Robison and G. D. Jarvinen,"Water-Soluble Metal-Binding Polymers with Ultrafiltration: A Technology for the Removal, Concentration, and Recovery of Metal Ions from Aqueous Streams", ACS Symposium Series volume, *Advances in Metal Ion Separation and Preconcentration*, R. Rogers, A. Bond and M. Dietz eds, Chap. 20, pp 294-330, 1998.

Lisa Colletti, George Havrilla, "Trace Element Detection with Micro-x-Ray Fluorescence", Advances in X-Ray Analysis, Vol 44, **1999**.

Darin E. Kizer, R. Bryan Miller, and Mark J. Kurth. Fused Pyrazolo Heterocycles: Intramolecular [3+2]-Nitrile Oxide Cycloadditions Applied to Syntheses of Pyrazolo[3,4-g][2,1]dihydrobenzoisoxazol(in)es. Tetrahedron Letters, 40: 3535-38, 1999.

Robert E. Sammelson, R. Bryan Miller, and Mark J. Kurth. The Synthesis of Tetraheterocyclic Polyisoxazole Chelating Ligands Using the Intermolecular 1,3-Dipolar Cycladdition Reaction. Journal of Organic Chemistry. In-Prep.

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

Project ID: 64947

Calvin C. Ainsworth, Pacific Northwest National laboratory

Benjamin P. Hay, Pacific Northwest National Laboratory
Samuel J. Traina, Ohio State University
Satish C. B. Myneni, Lawrence Berkeley National Laboratory

Research Objective

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

1. To develop an understanding of the interactions between siderophores (and their functional moieties), Fe and actinide oxides, their surface chemical properties that foster their dissolution and the conditions that maximize that dissolution.
2. To develop the computational tools necessary to predict the reactivity of different siderophore functional groups toward oxide dissolution and actinide(IV) solubilization.
3. To identify likely candidate chelates for use in decontamination processes.

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

Research Progress and Implications

This report summarizes research after 1.5 years of a 3-year project. Initial investigations have centered on dissolution, computational chemistry and XAS; XAS results (S. Traina) are reported elsewhere.

Dissolution studies to date have concentrated on the hydroxamic acid-type ligands with one, two and three hydroxamate functional groups; acetohydroxamate; rhodotorulic acid; and desferrioxamine B. Batch-type pH-stat investigations have shown dissolution rates of iron oxides (geothite, hematite, and magnetite) increase by more than an order of magnitude as the number of functional groups per molecule increase (i.e., acetohydroxamate, rhodotorulic acid, and desferrioxamine B) even though

the total concentration of hydroxamic acid groups remain constant. Unlike oxide dissolution in the presence of ethylenediaminetetraacetic acid (EDTA), Fe oxide dissolution rate appears to decrease linearly as pH is increased from 4.5 to 9.0. This suggests that, unlike EDTA, there is limited binuclear adsorption of the ligand, or readsorption of the dissolved Fe-siderophore at low pHs when the surface is positively charged. These results will be reported at the EMSP workshop in April.

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

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

Planned Activities

Dissolution studies will focus on catecholamide siderophores that have been isolated from selected organisms. In addition, several catecholates are being synthesized to systematically test the MM3 model discussed above. Investigations will continue to focus on the Fe oxides (geothite, hematite, and magnetite). However, studies of UO_2 dissolution will begin at the end of this year and continue in the final year of this project. Modeling efforts will continue to expand to include the hydroxamate

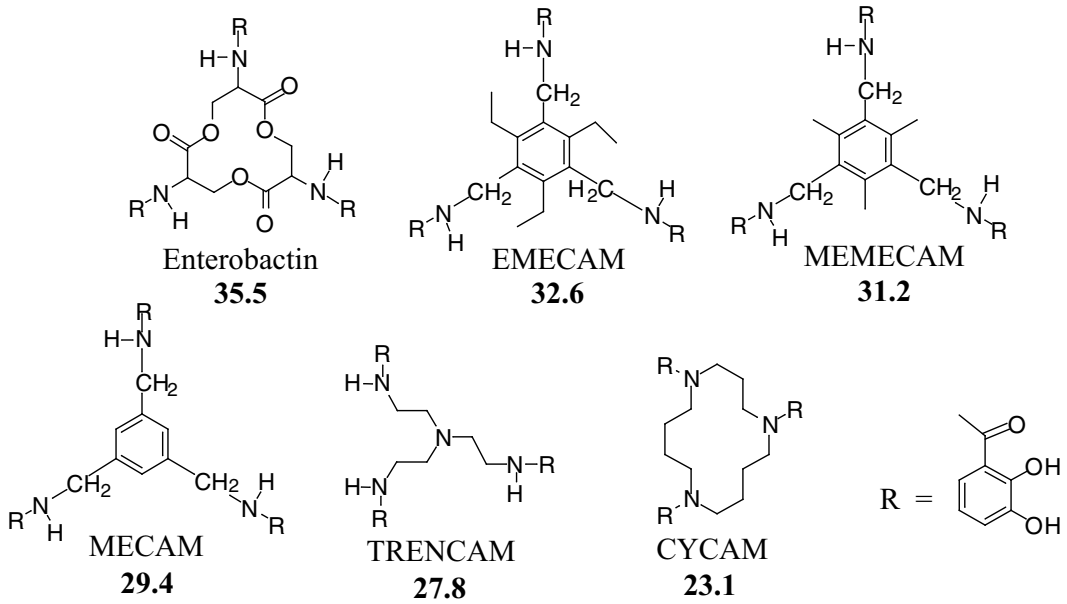


Figure A. **The six tris-catecholamide siderophore architectures that have been examined using the developed model. Relative affinities for Fe(III) are given as pFe values (10_M ligand, 1_M Fe(III), and pH 7.4).**

siderophores. To date, the optical spectroscopy investigations have not progressed as anticipated but will continue and these efforts will be integrated with the XAS investigations of S. Traina and S. Myneni.

Development of Monitoring and Diagnostic Methods for Robots Used in Remediation of Waste Sites

Project ID: 60040

Michael Martin, Foster Miller Technologies, Inc

Executive Summary

In the Environmental Restoration and Waste Management Program of the Department of Energy (DOE), extensive use of robots is planned for safe and efficient clean up of hazardous and radioactive waste sites. Robots operating at these waste sites will be exposed to a variety of life-limiting environmental and operational conditions. Undetected faults in these robots can have serious consequences including damage to the waste containment facilities by the faulty robot, complete or partial failure of the robots which could result in delays in the clean up activities, or in extreme cases could result in loss of the robot.

In this research proposal, to avoid the dangers associated with in-operation failure of robots, Mechanical Technology Inc. (MTI) and Rice University (RU) propose to develop Monitoring and Diagnostic (M&D) methods which would provide for early stage detection, isolation, and tracking of developing faults before they result in serious failure. Efficient M&D methods developed in this research would help the DOE personnel in reducing the risk of catastrophic in-site robot failures and thereby decrease the risk of damaging the containment facilities, loss of robot, and mission failures. By avoiding the additional time and cost required for post-robot-failure clean up, the M&D methods will help in providing for faster, safer, and less expensive clean up.

To perform M&D of robots, presently there are several applicable methods available in the literature which have been proven to provide early detection of incipient faults. However, all of these methods are limited in application to electrically driven robots. The utility and effectiveness of these methods in application to remediation robots, which are typically hydraulic in nature, have never been proven. The research in this program will be a pioneering effort for developing efficient M&D methods for hydraulic robots, with applications to a wide variety of robots including remediation robots, multi-arm manipulators, and industrial robots.

The work in this program is based on the extensive study undertaken in a different DOE program to analyze the M&D needs of remediation robots. In this study, the Rosie Mobile Worksystem, developed by RedZone Robotics and Carnegie Mellon University for operation in nuclear environments was selected as a reference. A failure modes and effects analysis was performed to identify various failure modes due to environmental and operational conditions, their cause and effect on the overall system performance, and the criticality, speed, and probability of failures. This analysis indicated that faults in the Hydraulic Power Supply Subsystem (HPSS) and the Tether Drive Subsystem of Rosie were the most critical for which M&D methods are needed. In the research, these M&D methods will be developed by assembling a test rig at MTI test laboratories for performing seeded-fault experiments. This test rig will be composed of a HPSS and an Actuator Subsystem which is representative of most of the typical actuators in Rose. A variety of faults originating due to radiation, corrosion, dust, fluid contamination, etc. will be installed in the test rig, and signals from nine different sensors will be used to provide early detection of faults.

To develop efficient M&D methods for remediation robots, the research will address two main challenges: (1) effective differentiation of changes in sensor signals due to faults from those due to robot dynamics in presence of noise and fault signature variability, and (2) quantification of the complex interactions between various components for fault isolation. The dynamic operation of the robot changes the sensor signals making it difficult to distinguish these changes from those caused by a fault. The task is further complicated by external noise in the sensor signal and fault signature

variability due to the complex interactions between the robot and its environment. The research will investigate various dynamic model-based methods, fuzzy and dynamic thresholding methods, and pattern classification methods that can provide clear and early indication of faults in the robot by coping with robot dynamics, sensor noise, and fault signature variability. The second challenge the research will address relates to the complex interactions between various components in the robot and its environment that causes problems in differentiating the faulty components from their secondary effects. In the research, various expert system approaches based on fault trees and fuzzy knowledge representation will be investigated to identify the most effective means of identifying faults in remediation robots.

Basic Engineering Research for D&D of R Reactor Storage Pond Sludge: Electrokinetics, Carbon Dioxide Extraction, and Supercritical Water Oxidation

Project ID: 64979

Edward A. Hamilton, Strom Thurmond Institute

Dr. David A. Bruce, Clemson University
Dr. Lawrence Oji, Savannah River Technology Center
Dr. Ralph E. White, University of South Carolina
Dr. Michael A. Matthews, University of South Carolina
Dr. Mark C. Thies, Clemson University

Research Objective

Collaborating researchers at the University of South Carolina (USC), Clemson University (CU), and the Savannah River Site (SRS) are investigating the fundamentals of a combined extraction and destruction process for the decontamination and decommissioning (D&D) of PCB-contaminated materials as found at DOE sites. Currently, the volume of PCBs and PCB-contaminated wastes at DOE sites nationwide is approximately 19,000 m^3. While there are a number of existing and proposed processes for the recovery and/or destruction of these persistent pollutants, none has emerged as the preferred choice. Therefore, this research focuses on combining novel processes to solve the problem. The research objectives are to investigate benign dense-fluid extraction with either carbon dioxide (USC) or hot water (CU), followed by destruction of the extracted PCBs via either electrochemical (USC) or hydrothermal (CU) oxidation. Based on the results of these investigations, a combined extraction and destruction process that incorporates the most successful elements of the various processes will be recommended for application to contaminated DOE sites.

Research Progress and Implications

This report summarizes work after nine months of a three-year project. This project involves personnel from two Universities and the SRS. Bi-monthly progress reports are submitted to SCUREF, and quarterly meetings at alternating sites have been held to share progress, make presentations, and plan future activities.

At USC, tracer diffusion experiments have been conducted with model contaminants, including some chlorinated compounds. Two papers are being prepared on the tracer work. The supercritical carbon dioxide extraction system is up and running, including two ISCO syringe pumps, allowing continuous extraction. A promising surfactant has been chosen and is on-hand for initial extraction experimentation. A search is underway to find additional commercially available surfactants that are both soluble in supercritical carbon dioxide and UV-detectable. A schematic of the extraction system is shown in Figure I.

A high-pressure cell for electrochemical destruction experiments has been constructed. Complications have arisen concerning high-pressure sealing of electrodes and manufacture of a custom high-pressure cell. Electrolytes will be added to the system to enhance the conductivity in carbon dioxide. One new electrolyte has been synthesized and additional electrolytes are being researched. A schematic of the electrochemical reaction system is given in Figure II. Some commercially available PCB surrogate compounds have been chosen and ordered for initial extraction and electrochemical experiments. A gas chromatograph has been prepared for PCB analysis and

will be used to evaluate both extraction and electrochemical destruction results. In addition, a dialogue has been initiated with University Health and Safety officers to discuss the special requirements and hazards associated with working with PCBs.

At CU, a supercritical water oxidation (SCWO) reactor design has been completed. The design includes a specialized mixing tee, which will be custom designed and fabricated at Clemson. The heat source for the reactor, a Techne sand bath oven, has been installed and is being optimized for the desired experimental conditions. Heat transfer analyses have revealed the depth to which the reactor coil should be immersed into the sand bath and customized holding brackets are being designed. A schematic of the SCWO reactor is given in Figure III. A Hewlett-Packard mass spectral analyzer has been ordered. The analyzer is planned for installation and operation in June 1999, and to be connected to a PC for control and data acquisition. Drawings have been developed for a high-pressure view cell with variable path lengths. This vessel will be used for in-situ measurements of PCB solubility at elevated pressures in hot and supercritical water if existing equipment proves insufficient.

SRS personnel have been providing support to the project by attending all quarterly meetings, providing regulatory compliance information regarding PCB handling and usage, and providing model matrix material. This model material, used in the field to absorb PCB-contaminated liquids, will be contaminated in the lab and used for extraction experiments.

Planned Activities

USC:

Summer 1999: Finish construction and pressure testing of electrochemical cell
Begin basic conductivity experiments and cyclic voltammetry
Explore the use of electrolytes to enhance carbon dioxide conductivity
Compile voltammetry data and analyze system effectiveness and efficiency
Explore purchase and implementation of a new electrochemical batch reactor provided from a commercial vendor
Begin extraction experiments with surrogate compound(s) and surfactant
Perform extraction experiments with model matrix materials provided by SRS
Continue to search for additional surfactants based on initial extraction results
Continue extraction experiments

Long Term: Design a continuous-flow electrochemical destruction system
Determine PCB destruction efficiencies / kinetics, correlate data, prepare models
Perform PCB + surfactant extraction experiments

CU:

Summer 1999: Continue literature search for SCWO and PCB solubility data
Connect mass spectrometer for reaction byproduct analysis
Fine tune heat transfer model
Build custom mounting bracket and reactor assembly

Long Term: Begin PCB solubility experiments
Construct SCWO system
Examine oxidation reaction kinetics
Compare the performance of different oxidizing agents (O_2 vs. H_2O_2)

Information Access

Publications and Presentations

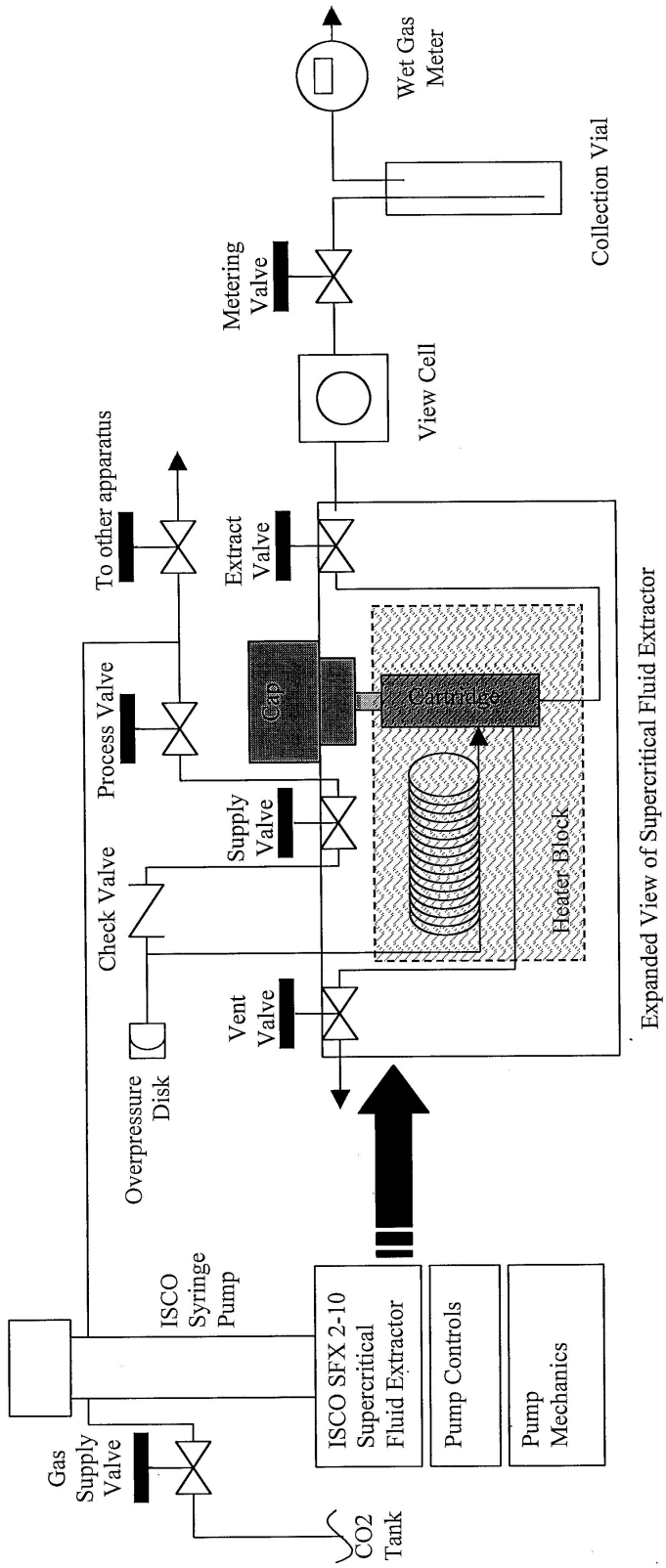
"Decontamination & Decommissioning of PCB Sites at SRS." J. Pickett, L. Oji, M. Matthews, R. White, J. Weidner, D. Bruce, M. Thies. Poster paper given at the Workshop on Integration of End User Needs with Research Projects for the Environmental Management Science Program, Savannah River Site, November 17-18, 1998.

"Mass Transfer in CO_2/Surfactant Systems", M. Matthews, Presented at the 1998 AIChE Annual Meeting, Miami Beach, FL, November 15-20, 1998.

"Sonochemical Oxidation of Organic Contaminants in Waste Water", Bruce, D., Presented at the AIChE Annual Meeting, Miami Beach, FL, November 15-20, 1998.

Figure I

Supercritical Carbon Dioxide Extraction Apparatus



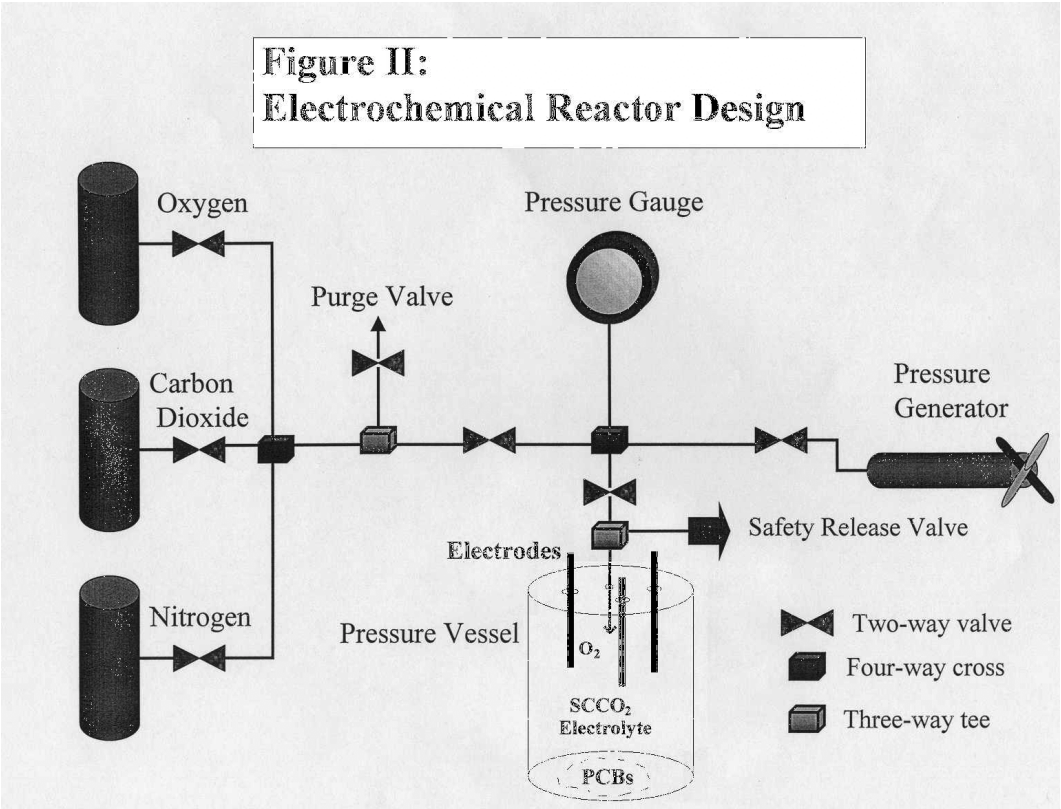


Figure II:
Electrochemical Reactor Design
Oxygen
Pressure Gauge
Purge Valve
Carbon Dioxide
Pressure Generator
Safety Release Valve
Electrodes
Nitrogen
Pressure Vessel
O_2
$SCCO_2$ Electrolyte
PCBs
Two-way valve
Four-way cross
Three-way tee

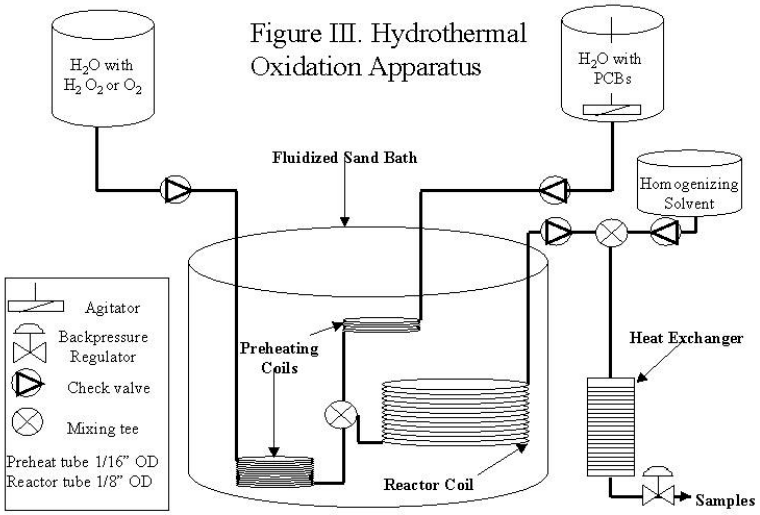


Figure III. Hydrothermal Oxidation Apparatus
H_2O with H_2O_2 or O_2
H_2O with PCBs
Fluidized Sand Bath
Homogenizing Solvent
Agitator
Backpressure Regulator
Check valve
Mixing tee
Preheat tube 1/16" OD
Reactor tube 1/8" OD
Preheating Coils
Heat Exchanger
Reactor Coil
Samples

Three-Dimensional Positron-Sensitive Germanium Detectors

Project ID: 65015

Dr. Mark Amman, Lawrence Berkeley National Laboratory

Research Objective

A critical component of the DOE decontamination and decommissioning effort is the characterization of radioactively contaminated equipment and structures. Gamma-ray spectroscopy and imaging with germanium (Ge) based detectors are powerful techniques that allow for the quick and accurate in-situ identification, spatial mapping, and quantification of radioactive contaminants. However, the image resolution obtained with a Ge detector can be limited by the accuracy to which the gamma-ray interaction events are spatially detected within the detector itself. Our primary objective is to develop the technologies necessary to produce Ge gamma-ray detectors with enhanced accuracy in locating gamma-ray interaction events thereby resulting in improved image resolution. Our approach is to locate the gamma-ray interaction events within the detector in all three dimensions rather than just two. Additionally, we will base the detectors on LBNL fabrication technologies and work to develop the simplest possible detector geometries and signal-readout electrode structures in order to reduce the system complexity and difficulties in fabrication. The technologies developed as a result of this research will form the basis for the design and construction of future high-performance gamma-ray imaging systems. These instruments will greatly facilitate DOE's radioactive materials characterization process.

Research Progress and Implications

This section summarizes the work from the initial 17 months of our three-year project. During this period, we have concentrated our efforts on three separate task areas: detector fabrication development, orthogonal-strip detector fabrication and testing, and detector modeling. The progress made in each area and the importance of the work are given below.

Key to the success of gamma-ray imaging with Ge detectors is the development and use of cost-effective, robust detector fabrication processes. Such processes have been developed previously at LBNL and, through this project, are being further refined for the specific needs of this application. In our detectors, the electrical contacts to the bulk single-crystal Ge are made through an RF sputtered amorphous semiconductor (normally Ge or silicon (Si)) layer deposited onto the bulk Ge. These contacts allow for the application of the high voltages necessary to fully collect the electrons and holes generated by gamma-ray interaction events within the bulk Ge and for the measurement of the electrical signals produced by this charge collection. These electrical signals form the basis for the determination of each gamma ray's energy and interaction location thereby allowing spectroscopy and imaging to be performed. The amorphous semiconductor contacts typically consist of an amorphous semiconductor layer that covers much of the detector surface. On top of this layer is deposited a metal electrode layer to which an electrical connection can be made. To produce a detector capable of imaging, the metal layer is segmented (divided into a number of pieces), and an electrical connection is made to each segment. For high spatial resolution, these electrodes will be finely spaced. A challenge is then to electrically connect each of these finely spaced electrodes to the measurement electronics. We have accomplished this task by developing a metallization/wire bonding process that allows us to make contact to these closely spaced (< 1 mm) electrodes on Ge detectors without damaging the detector. This high-yield process has now been successfully used on a number of detectors.

Achieving specific properties in the amorphous contact layer is also crucial to the proper performance of the detector. In particular, both a large electrical barrier to charge carrier injection and a specific film resistivity are necessary. We have systematically studied the injection barrier properties of amorphous Ge and amorphous Si films deposited under various conditions onto bulk Ge. From this work we know that amorphous Ge sputtered in pure argon produces a contact that works nearly equally well as a barrier for both hole and electron injection and can therefore be used for either a positively or negatively biased electrical connection. Also, if necessary, a greater hole barrier to injection can be obtained (with a correspondingly reduced electron injection barrier) from amorphous Ge sputtered in a hydrogen-argon mixture. Similarly, a greater electron barrier is obtained from Si sputtered in pure argon. The resistivity of the amorphous films depends on the type of film (either Ge or Si) and the amount of hydrogen incorporated into the film as dictated by the sputter gas mixture and the residual gases in the sputter chamber. An increase in resistivity by orders of magnitude is obtained by incorporating hydrogen into the films. We are presently working to understand the effect that this film resistivity has on the detector performance and will optimize the film based on this newly gained understanding.

With the aid of the above fabrication process development, we have produced small prototype Ge detectors. The objectives of this task have been to test and refine the fabrication processes, study the physics of charge collection and signal formation in highly segmented Ge detectors, and investigate depth-of-interaction sensing. An orthogonal-strip type geometry was chosen for these detectors because of its simplicity. In this geometry the electrodes on one side of a planar detector are segmented into a set of linear strips. On the opposing detector surface is another set of strips that run perpendicular to the first set. The location of a gamma-ray interaction event within such a detector is determined by measuring the induced charge signals from each strip of both sets of electrodes. For a simple gamma-ray interaction event, a single strip on one side of the detector will collect the generated holes, and a single strip from the opposing detector surface will collect the electrons. Therefore, for such an event, only one strip on each side of the detector will produce a net charge signal thereby localizing the interaction event in two dimensions. To locate the interaction event more precisely, we desire to also determine the depth at which the gamma ray has interacted within the detector thereby producing a three-dimensional position-sensitive detector. We have accomplished this by measuring the difference between the arrival time of the holes at a strip on one side of the detector and the arrival time of the electrons at a strip on the opposing detector side. We have successfully demonstrated a depth position resolution of about 0.25 mm for 60 keV gamma rays. The eventual use of this technique for gamma-ray imaging should allow for the more accurate spatial mapping of radioactive contaminants. This work has been summarized in reference 1.

In addition to high position sensitivity, it is also important that the detector be efficient and have excellent energy resolution. From tests with an orthogonal-strip detector, we see evidence of a loss of energy resolution and photopeak efficiency for gamma rays interacting in the region between two adjacent strips. Based on these measurements and modeling results, it appears that this is caused by slow charge collection in a weak field region between adjacent strips. This loss of efficiency would degrade detector performance. One method to solve this poor charge collection problem is to increase the field between adjacent strips. This can be accomplished by using only every other strip for signal measurement. The remaining strips are used as field-shaping electrodes to which a voltage can be applied thereby increasing the field between adjacent strips and improving the charge collection to the signal measurement strips. We have successfully used this technique to improve the photopeak efficiency and energy resolution of our orthogonal-strip detector (see reference 1). However, from preliminary measurements, it also appears that this charge collection problem can be substantially reduced without the field-shaping electrodes simply by using an optimized amorphous semiconductor contact layer. We are presently investigating this method.

The spectroscopy and imaging performance of the Ge detectors depends on the detector and electrode geometry and the readout electronics configuration. Numerical modeling is an efficient means to optimize the detector and readout electronics design for the best possible system performance. We are presently modeling the response of orthogonal-strip detectors in order to refine the detector design and to allow us to devise the most effective readout electronics. These calculations combined

with our measurements will be used to determine the best method to electronically extract the gamma-ray interaction position from the measured induced charge signals.

Planned Activities

In the short term we plan to continue the investigation with small orthogonal-strip detectors concentrating on improving energy resolution, photopeak efficiency, and position sensitivity. We will also continue the development of a specialized cryostat and electronics for the more thorough measurements required to accomplish the detector development tasks.

In both the short term and long term, our efforts will continue to be directed at refinements in the fabrication processes. We will also continue the development and use of modeling tools to better understand the physics of our detectors and to optimize their performance. Combined with this work will be the development of improved detector designs and readout electronics.

Once a good understanding has been gained from modeling and measurements made with small detectors, we will design, fabricate, and test larger area detectors more suitable for imaging applications.

Information Access

1. "Three-Dimensional Position Sensing and Field Shaping in Orthogonal-Strip Germanium Gamma-Ray Detectors," M. Amman and P. N. Luke, Nucl. Instr. and Meth. A, accepted for publication.
2. "Germanium Orthogonal Strip Detectors with Amorphous-Semiconductor Contacts," P. N. Luke, M. Amman, B. F. Phlips, W. N. Johnson, and R. A. Kroeger, IEEE Trans. Nucl. Sci., submitted for publication.

Advanced Sensing and Control Techniques to Facilitate Semi-Autonomous Decommissioning of Hazardous Sites

Project ID: 55052

Robert J. Schalkoff, Clemson University

Robert. M Geist, Clemson University
Darren Dawson, Clemson University

Research Objective

This research is intended to advance the technology of semi-autonomous teleoperated robotics as applied to Decontamination and Decommissioning (D&D) tasks. Specifically, research leading to a prototype dual-manipulator mobile work cell is underway. This cell is supported and enhanced by computer vision, virtual reality (VR) and advanced robotics technology. The overall goal of this phase of the research is to autonomously generate a specification of scene geometry using a stereo pair of camera images sufficient to produce a virtual replica of the sampled scene that is suitable for VR rendering and subsequent real-time robotic D&D operations, navigation, planning, and mission training.

Research Progress and Implications

This report summarizes work after 3.5 years of a 3-year project (no-cost extension of the above-referenced project for a period of 12 months granted).

The fourth generation of a vision sensing head for geometric and photometric scene sensing has been built and tested. Currently, we are developing estimation algorithms for automatic sensor calibration updating under robot motion.

We have modified the geometry extraction component of the rendering pipeline. Laser scanning now produces highly accurate points on segmented curves. These point-curves are input to a NURBS (non-uniform rational B-spline) skinning procedure to produce interpolating surface segments. The NURBS formulation includes quadrics as a sub-class, thus this formulation allows much greater flexibility without the attendant instability of generating an entire quadric surface. We have also implemented correction for diffuse lighting and specular effects.

The QRobot joint level control was extended to a complete semi-autonomous robot control system for D&D operations.

Currently, the project is at the critical stage where the three subsystems (imaging, VR and robotics) are being integrated and tested. We have also had extensive discussion with INEEL personnel who have expressed interest in this work in conjunction with the DOE DDROPS effort.

Planned Activities

Future research focuses on achieving the originally-stated project goals. This includes the synergistic integration of several emerging technologies. Specifically, we are combining fundamental manipulator control research with visual feedback/virtual reality research and applying the technologies to an industrial PUMA 560 robot manipulator. We plan a laboratory demonstration during the Summer of 2000.

Information Access

Publications

N. Costescu, M. Loffler, E. Zergeroglu, and D. Dawson, "QRobot – A Multitasking PC Based Robot Control System", Proc. of the IEEE Conference on Control Applications, Trieste, Italy, Sept., 1998, pp 892-896.

Geist, R., Vernon, D., and Schalkoff, R., "Rendering Inversion in the Automated Construction of Virtual Environments," Proc. 3rd ASCE Specialty Conf. on Robotics for Challenging Environments (ROBOTICS '98), Albuquerque, New Mexico, April, 1998, pp. 85 - 91.

Geist, R., Schalkoff, R., Stinson, T., and Gurbuz, S., "Autonomous Virtualization of Real Environments for Telepresence Applications," PRESENCE: Teleoperators and Virtual Environments, 6:6(1997), MIT Press, pp. 645 - 657.

Van Pernis, A., "Surface Construction from within a Virtual Environment," Proc. 37th Annual ACM Southeast Conf., Mobile, Alabama, April, 1999. NOTE: this was the winning paper in the ACM SE student paper competition.

Web Page(s)

Our web page coverage of this activity may be found at the URL **http://ece.clemson.edu/iaal/doeweb/doeweb.htm.**

"Green" Biopolymers for Improved Decontamination of Metals from Surfaces: Sorptive Characterization and Coating Properties

Project ID: 64907

Dr. Brian H. Davison, Oak Ridge National Laboratory

Dr. Tanya Kuritz, Oak Ridge National Laboratory

Research Objective

The proposed research aims to develop a fundamental understanding of important biological and physical chemical parameters for effective decontamination of metal surfaces using environmentally benign aqueous-based biopolymer solutions. Understanding how heavy metal–chelating biopolymers coat and interact with contaminated surfaces will benefit the development of novel, safe, easy-to-apply decontamination methodologies for removal of radionuclides and heavy metals. The benefits of these methodologies will include the following:

- decreased exposure hazards for workers;
- decreased secondary waste generation;
- increased efficiency of decontamination;
- positive public appeal and development of novel, nature-friendly business opportunities; and
- lower cost of cleanup to the government.

We propose to use aqueous biopolymer solutions to coat a contaminated metal surface (i.e., steel), solubilize the heavy metals (e.g., uranium) from the surface, and bind the heavy metals into the biopolymer. The biopolymer coating (containing the immobilized hazardous metal contaminants) will then be removed as a viscous film, as a dry powder, or by washing. This "apply, wait, and remove" procedure will reduce the amount of worker time spent in decontamination activities.

Research Progress and Implications

This report summarizes work after 16 months of a 3-year project. The research aims to develop a fundamental understanding of important parameters for effective decontamination using aqueous biopolymer solutions. The work may be broken down into three parts: (1) selection and generation of biopolymers; (2) characterization of sorbent and material properties; and (3) study of transport properties. Metals used include U, Cu, Cd, and Fe. The latter three of these are model non-radioactive heavy metals that have quickened the pace of laboratory studies in the first and early second year. Critical experiments during the second (and third) year are being performed using depleted uranium.

Screening. We have screened several biopolymers for metals sorption by cultivating a variety of algae (cyanobacteria). Algal strains screened include: *Nostoc* sp. strain GSV39, *Nostoc* sp. strain GSV40, *Nostoc muscorum* (collection of Ukrainian Institute of Hydrobiology), *Anabaena* (*Nostoc*) sp. strain PCC7120, and *Phormidium mucicola* SLR1. These cultures were grown in photobioreactors for 5 days with two different media, then left to mature (maturation leads to accumulation of copious polymer) for 1 month. Biomass was collected and dried. Dry biomass was reconstituted in nitrate buffer and used for metal-binding experiments. The polysaccharides can be partially purified into soluble and insoluble fraction with different rheological properties.

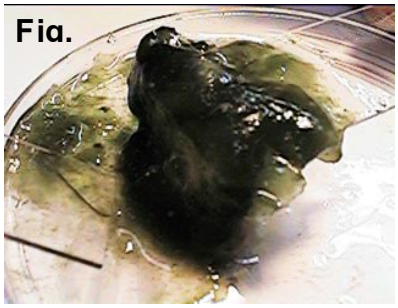


Fig 1

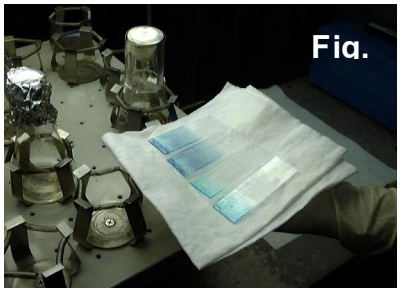


Fig 2

Fig. 1 shows the abundant synthesis of biopolymers by alge (*Nostoc* sp. GSV40). In Fig. 2, a bone-gel biopolymer was used to coat a glass slide and exposed to a solution of copper nitrate. The copper was sorbed from the solution into the gel on the surface – as shown by the blue tint. Algae are growing in shakeflasks in the background.

The soluble excretable biopolymer fraction, which can also serve as a metal chelator was precipitated from media with 2 volumes of cold ethanol. Both components are being analyzed for metal-binding properties.

Selection. The materials/polysaccharides, both soluble and insoluble, isolated from ***Nostoc muscorum Ag*** were chosen for continuation of metal sorption studies after initial screening studies. These materials displayed the strongest binding characteristics for Cd, Fe, Cu, and U (data not shown).

Preparation of Contaminated Steel Coupons. Steel coupons were coated with uranium (UO_2^{+2}) as a means of mimicking actual contamination conditions. Literature protocols for coupon size, shape, cleaning, and heavy metal application were combined and experimentally refined for this project. Techniques for direct measurement of alpha radiation (counts of U^{+6}) on the surface of the coupon, in addition to ICP determinations of U^{+6} in solution and traditional mass balance methods, were developed and verified. This is critical to quantify contaminant removal.

Planned Activities

Quantities of the best metal-sorbing biopolymers will be produced. We will continue tests of heavy metal removal via sorption and adhesion from controlled contaminated steel coupons, primarily with depleted uranium. Radioactive disintegration and inductively coupled plasma spectroscopy (ICP) will be used to quantitate the removal and isotherms. We will test the physical "gel" properties for use as a coating.

Tasks: Green Biopolymers	**Year 1**				**Year 2**						**Year 3**			
Selection/production of biopolymers														
Characterization of metal-chelation properties														
Metal removal from surfaces by biopolymer														
Methods of biopolymer surface application														

Information Access

"Green Biopolymers for Decontamination" – poster presentation at "Workshop on integration of end user needs with research projects for EMSP: Focus on Deactivation and Decommissioning" at Savannah River Site on Nov. 17-18, 1998.

Presentation, “Green Biopolymer for Decon of Contaminated Surfaces” delivered at *Decontamination, Demolition and Restoration (DD&R) Topical Meeting on Site Restoration of Government and Commercial Facilities*, Sep. 12-16, 1999, Knoxville, TN.

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

Project ID: 64931

Yuri A. Gorby, Pacific Northwest National Laboratory

Gill G. Geesey, Montana State University
Frank Caccavo, Jr., University of New Hampshire
James K. Fredrickson, Pacific Northwest National Laboratory

Research Objective

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

Research Progress and Implications

This report summarizes accomplishments after 1.5 years of a 3 year project. Significant advances have been realized in each aspect of the proposed research.

The research is structured into four primary tasks that are being addressed by members of the collaborative team. Task 1 investigates the factors controlling the attachment to and release from oxide scale that forms on corroding mild and stainless steel by metal-reducing bacteria. Task 2 probes the effects of iron oxide composition and surface properties on cell attachment and biofilm formation. Task 3 examines and quantifies the reductive dissolution of synthetic iron oxide thin films as well as the reductive dissolution of iron oxide scale on corroding steel in the presence and absence of soluble electron shuttles that can enhance the rate and extent of enzymatic iron reduction. Task 4 determines the distribution of actinides released from Fe oxides during reductive dissolution of scales that are colonized by metal-reducing bacteria. Particular attention will be given to the processes that direct the incorporation of actinides into the biomass. Due to the brief format of this report, results and major implications are summarized to provide a generalized summary of salient points. This research is providing information necessary for developing optimal approaches for (1) delivering and distributing cells to contaminated corrosion films, (2) determining the fate of contaminants impacted by attached bacteria, and (3) recovering contaminants for further processing

I. *Reduction and fate of Pu(IV) by metal reducing bacteria.* Iron reducing bacteria were tested for their ability to reduce insoluble Pu(IV), provided as PuO_2, to soluble Pu(III). The fate of Pu(III) was determined using neodymium, Nd(III), as a non-radioactive analogue. The significant results demonstrated:

1. Iron reducing bacteria enzymatically reduced insoluble Pu(IV) to Pu(III).
2. At pH values approaching 6, Pu(III) sorbed to cell surfaces.
3. Cell biomass provides a significant sink for accumulation of actinides.

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

II. *Cell attachment*. Adhesion of the iron reducing bacterium *Shewanella alga* strain BrY to hydrous ferric oxide, goethite, and hematite was examined. The results demonstrated that:

1. The bacteria readily adhere to both crystalline and amorphous Fe(III) oxide surfaces.
2. Adhesion of *S. alga* strain BrY to hydrous ferric oxide (HFO) was correlated with ionic strength, and thus was accurately described by the DLVO theory.
3. Rate of solid phase iron reduction was directly correlated with adhesion of cells with surfaces and, hence, with ionic strength of the medium.

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

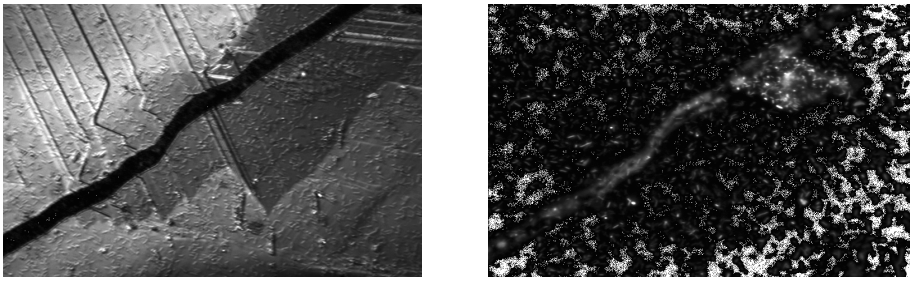


Figure 1. Images taken on a (001) hematite surface of strain *S. putrefaciens* strain MR1 (p519nGFP) after 52 h. Bright cells are particularly associated with the step edge. DIC images (left) were captured using an exposure of 32 msec, epifluorescence images (right) with an exposure of 7 sec. Gain for all images was 4 dB.

Results from this work demonstrated that:

1. Primary cells adhesion occurred through flagellar attachment
2. Cells were heterogeneously distributed on hematite surfaces, with preferential attachment observed at cracks, steps, and crystal defects
3. Luminescence was greater with cells attached at the cracks, steps and defects, suggesting that cells were metabolically active at these sites.

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

1. Cells treated in this manner formed small (100 nm) vesicles on the cells surface.
2. Cells began to detach from the mineral surface

Vesicles remained attached to the mineral surface.

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

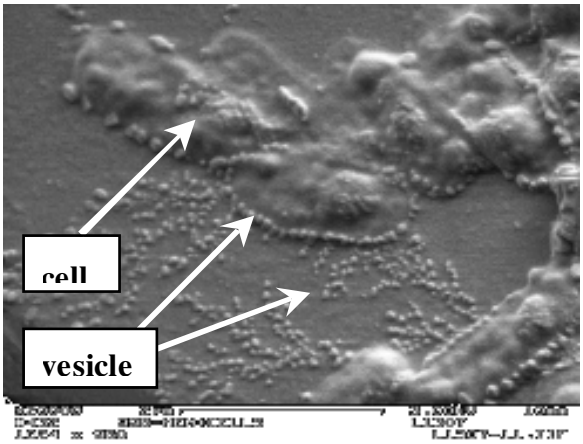


Figure 2. SEM image of bacterial cells with attendant vesicles on a hematite crystal.

Planned Activities

The remainder of the project will focus on:

1. Describing the role vesicles play in radionuclide reduction and accumulation
2. Optimizing conditions for biomass/radionuclide recovery
3. Evaluating decontamination of activated corrosion films

Proposed research is expected to be completed within the timeframe of the project.

Information Access

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

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

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

Development of Novel, Simple, Multianalyte Sensors for Remote Environmental Analysis

Project ID: 65001

Dr. Sanford A. Asher, University of Pittsburgh

Research Objective

We will develop simple, inexpensive new chemical sensing materials which can be used as visual color test strips to sensitively and selectively report on the concentration and identity of environmental pollutants such as cations of Pb, U, Pu, Sr, Hg, Cs, Co as well as other species. We will develop inexpensive chemical test strips which can be immersed in water to determine these analytes in the field. We will also develop arrays of these chemical sensing materials which will be attached to fiber optic bundles to be used as rugged multichannel optrodes to simultaneously monitor numerous analytes remotely in hostile environments.

These sensing materials are based on the intelligent polymerized crystalline colloidal array (PCCA) technology we recently developed. This sensing motif utilizes a mesoscopically periodic array of colloidal particles polymerized into an acrylamide hydrogel. This array Bragg diffracts light in the visible spectral region due to the periodic array of colloidal particles. This material also contains chelating agents for the analytes of interest. When an analyte binds, its charge is immobilized within the acrylamide hydrogel. The resulting Donnan potential causes an osmotic pressure which swells the array proportional to the concentration of analyte bound. The diffracted wavelength shifts and the color changes. The change in the wavelength diffracted reports on the identity and concentration of the target analyte.

Our successful development of these simple, inexpensive highly sensitive chemical sensing optrodes, which are easily coupled to simple optical instrumentation, could revolutionize environmental monitoring. In addition, we will develop highly rugged versions, which can be attached to core penetrometers and which can be used to determine analytes in buried core samples.

Research Progress and Implications

This report summarizes work after nine months of a three year project. We have developed a new method to crosslink our PCCA sensing materials with disulfide bridges. We cleave these bridges which then yield thiols which complex with heavy metals. We have demonstrated sensing of As(III). We are now investigating the utility of this sensing material for other heavy metals and are attempting to template the recognition sites for heavy metals.

Planned Activities

We are continuing on our plan to develop simple, inexpensive new chemical sensing materials which can be used as visual color test strips to sensitively and selectively report on the concentration and identity of environmental pollutants such as cations of Pb, U, Pu, Sr, Hg, Cs, Co as well as other species. We will develop inexpensive chemical test strips which can be immersed in water to determine these analytes in the field. We will also develop arrays of these chemical sensing materials which will be attached to fiber optic bundles to be used as rugged multichannel optrodes to simultaneously monitor numerous analytes remotely in hostile environments.

Information Access

The following references give further information on our chemical sensing materials.

"Intelligent Polymerized Crystalline Colloidal Array Hydrogel Film Chemical Sensing Materials", J. H. Holtz and S. A. Asher, Nature 389, 829-832 (1997).

"Intelligent Polymerized Crystalline Colloidal Arrays: Novel Chemical Sensor Materials," J. H. Holtz, J. S. W. Holtz, C. H. Munro, and S. A. Asher, Anal. Chem. 70, 780-791 (1998).

"Mesoscopically Periodic Photonic Crystal Materials for Linear and Nonlinear Optics and Chemical Sensing", J. Holtz, J. Weissman, G. Pan and S. A. Asher, Material Research Soc. 23, 44-50, (1998).

Metal Ion Analysis Using Near-Infrared Dyes and the "Laboratory-on-a-Chip"

Project ID: 64982

Greg E. Collins, Naval Research Laboratory

Qin Lu, Geo-Centers, Inc.

Research Objective

The primary objective of this project is to develop a sensitive and selective, portable sensor for radionuclides and heavy metals that utilizes a "laboratory-on-a-chip" platform for enabling low-cost, timely characterization of DOE remediation sites. This will be accomplished by synthesizing a new class of metal complexation ligands that are covalently linked to red fluorescing dyes, and utilizing these dyes for the selective quantitation of target metal pollutants through their selective separation down the microchannel of a "laboratory-on-a-chip." Inexpensive, compact light sources will be utilized as excitation sources, and detection will be achieved using compact, inexpensive, photodiode array detectors.

Research Progress and Implications

This work summarizes the present status as of March 1, 2000 for a 3 year project beginning October 1, 1998.

***Synthesis and characterization*:** To date, four different metal complexation ligands, cyclen, calix[6]arene, iminodiacetic acid (IDA) and 18-crown-6 have been successfully linked covalently to the fluorophore, rhodamine. Each of these molecules have been purified by column chromatography, and fully characterized by electrospray mass spectrometry. Our initial synthetic efforts have utilized rhodamine as the linkage fluorophore of choice, primarily because, unlike near-infrared dyes, they are an inexpensive alternative for deriving the experimental protocols necessary to covalently link the metal complexation ligands and fluorophores together. Three different covalent linkage schemes have been investigated: succinimidyl ester, isothiocyanate, and sulfonyl chloride. Rhodamine sulfonyl chloride has demonstrated the most success with respect to its reactivity and final product stability. Difficulties have been encountered in obtaining the desired product for reactions involving EDTA, presumably due to the reactivity of the carboxylic acid functional groups. We are currently pursuing protective groups to overcome this problem.

***Laboratory-on-a-Chip*:** Two separate microchip analysis platforms have been designed and fully interfaced to a computer for data collection, one for performing absorbance-based detection and the other for fluorescence. The absorbance-based detector utilizes a red LED light source and a photodiode array detector, while the fluorescence based system utilizes a green Nd:YAG laser and a miniature photomultiplier tube. Two metal complexation ligands, in particular, have demonstrated excellent promise with respect to the selective, microchip detection of uranium, and these will be discussed here.

With regards to fluorescence detection, rhodamine-calix[6]arene, a new, fluorophore tagged macrocycle synthesized in this program, has demonstrated excellent selectivity and sensitivity for the uranyl ion in the presence of a complex mixture of metal ions. Calixarenes form a barrel-shaped geometry which is well suited for uranyl ion metal complexation. The uranyl ion likely adopts a pseudoplanar penta- or hexa-coordinate structure that helps explain its enormous selectivity factors for uranium over other metal ions ($> 10^{12}$). It is for this reason that calix[6]arene has been coined the term, "super-uranophile." Our investigations on the microchip have established rapid separations

(< 50 sec) of the free ligand from the uranyl-complexed ligand. Furthermore, the addition of various transition, alkali and rare earth metal ions does not result in the formation of any additional separation peaks, thereby, verifying the high selectivity of this ligand for uranium.

Simple absorbance based detection methods are also being pursued based upon the commercially available metal complexation dye, Arsenazo III. This dye is particularly well-suited for adaptation to the laboratory-on-a-chip in this project due to its capability for lanthanide/actinide metal complexation, and the overlap of these metal complex absorbance peaks with the output of a red LED excitation source. Arsenazo III has the additional advantage of not complexing the vast majority of transition and alkali/alkaline earth metal ions which predominate at any remediation site. With citric acid in the separation buffer, we have demonstrated the selective separation of a mixture of uranium from three other lanthanides, Sm, Gd, and Ce in under two minutes. If EDTA is additionally added to the separation buffer, Arsenazo III will only complex colorimetrically to uranium, making its identification on a microchip very simple and highly selective.

Planned Activities

Efforts are currently focussed on quantitatively determining the various stability constants for metal complexation by the newly synthesized fluorophore-tagged ligands, in order to ascertain the impact of the fluorophore on metal complexation. While each ligand synthesized to date has had the fluorophore covalently linked directly to the metal complexation ligand, in the future we plan to synthetically introduce a short linkage or alkyl unit between the fluorophore and the ligand. This will help separate these two entities, improving our metal complexation and fluorescence properties. Following our experience gained with the reactivity of rhodamine, we are planning to transition to the synthesis of near-infrared fluorophore linked ligands in the near future. The separation and quantitation of metal ions by ligands generated from this program continue to be examined on both a commercial electrophoresis unit and on the “laboratory-on-a-chip” platform. Possible avenues of research include longer channel lengths and polyacrylamide deposition within the microchannels in order to improve resolution.

Real-Time Identification and Characterization of Asbestos and Concrete Materials with Radioactive Contamination

Project ID: 65004

Dr. George Xu, Rensselaer Polytechnic Institute

Dr. Xi-Cheng Zhang, Rensselaer Polytechnic Institute

Research Objectives

Concrete and asbestos-containing materials were widely used in U.S. Department of Energy (DOE) building construction in the 1940s and 1950s. Over the years, many of these porous building materials have been contaminated with radioactive sources, on and below the surface. This intractable radioactive-and-hazardous-asbestos mixed-waste-stream has created a tremendous challenge to DOE decontamination and decommissioning (D&D) project managers. The current practice to identify asbestos and to characterize radioactive contamination depth profiles involve bore sampling, and is inefficient, costly, and unsafe. A three-year research project was started on 10/1/98 at Rensselaer with the following ultimate goals: (1) development of novel non-destructive methods for identifying the hazardous asbestos in real-time and in-situ, and (2) development of new algorithms and apparatus for characterizing the radioactive contamination depth profile in real-time and in-situ.

Research Progress and Implications

a) Asbestos Identification

Asbestos cannot be identified by its chemical properties only. Existing methods, such as PLM and TEM, utilize mainly its optical properties, but have not been able to meet the requirements of real-time and *in-situ* applications in D&D. Novel methods will have to be developed to complement and to replace the existing methods.

Electro-optic Terahertz Time-domain Spectroscopy (EO THz-TDS) is a new technology being developed at Rensselaer's Ultrafast Optoelectronics Laboratory and elsewhere. The development of THz-TDS has opened this scientifically and technologically important, but long inaccessible spectroscopic region. The ultrawide bandwidth, coherence and sensitivity of this technique have been used to characterize the electronic, vibronic, and compositional properties of solid, liquid and gas phase materials, flames and flows. Many believe that research in this area could lead to a breakthrough that may eventually become as significant as ultrasound and X-ray technologies. Our expertise in optoelectronic and environmental engineering research allows us to propose innovative approaches to test that: each asbestos-containing sample has unique signatures which can be identified and characterized with the new THz time-domain spectroscopy method, and a unique electro-optic, far-infrared (FIR), electromagnetic (EM) field sampling and imaging system can be developed for real-time and in-situ applications.

As of 6/15/1999, the THz Imaging Laboratory has concentrated on the development of a unique THz imaging system. The short-term goal was to develop an adequate system with an ultrahigh sensitive and broad bandwidth for initial asbestos testing. A computer was purchased to control the system and to analyze the data. Necessary optical elements (in addition to the equipment that already exists at Rensselaer) were also purchased for the near-field THz sampling of asbestos at different optical wavelength. Testing of the system on limited asbestos samples has been done. Reference asbestos samples have been purchased to establish a library for benchmarking and testing. Preliminary results show that the signatures locate in a very broad range, especially when the concentration of

asbestos in the building materials vary significantly. This creates challenges in system design and sample classification. Issues have been identified for further investigation in the coming years. The prototype THz system and preliminary measurements have been presented at the Conference of Laser and Electro-Optics'99 at Baltimore, and Laser'99 at Munich.

b) Radiological Contamination Depth Profiling

This task is accomplished with relatively mature technology-gamma spectroscopy and Monte Carlo simulations. As of 6/15/1999, a non-destructive method based on *in-situ* gamma spectroscopy has been developed to determine the depth of radiological contamination in media. This method is based on our earlier work, Gamma Penetration Depth Unfolding Algorithm (GPDUA), which uses point kernel techniques to predict the depth of contamination from uncollided peak information. The GPDUA is designed and verified through extensive Monte Carlo simulations and validated through laboratory experiments. The method requires the a priori knowledge of the contaminant source distribution, which may be obtained from limited number of traditional bore sampling. The non-invasive method then will be extremely useful for quick scanning of large areas with deep contamination. It is estimated that this will reduce the time from weeks to one-day for a small building. The workers are much safer, because no air-radioactivity will be involved. The applicable radiological contaminants of interest are any isotopes that emit two or more gamma rays per disintegration or isotopes that emit a single gamma ray but have gamma-emitting progeny in secular equilibrium with its parent (e.g., ^{60}Co, ^{235}U, and ^{137}Cs to name a few). The predicted depths from the GPDUA algorithm using Monte Carlo N-Particle Transport Code (MCNP) simulations and laboratory experiments using ^{60}Co have consistently produced predicted depths within 5 % of the actual or known depth for a point-shaped contaminant. Several DOE users have expressed great interests in the technology, already no field testing has been arranged so far. A peer-reviewed paper for this research has been accepted for publication.

Planned Activities

From 6/15/1999 to 6/14/2000, we will systematically test asbestos materials with the THz system developed. We will study different types of asbestos such as chrysotile, amosite, crocidolite, and tremolite. We will consider concentration of asbestos in ACM ranging from 10% to 100%. Other environmental factors, such as moisture and impurity, will also be considered in the quality of sampling and identification. The roles of these sample conditions on the temporal and spectral distributions, as well as the sensitivity of the proposed method will be studied in detail. Realistic asbestos samples (e.g., transite panels) from DOE facilities will be investigated. Experiments involving both transmitted and reflected THz spectroscopy will be performed to establish a library of more definitive "finder prints" for the ACM most common in DOE. The optimal THz frequencies will be determined. Conventional analytical methods, such as PLM and ETM recommended by the EPA, will be utilized to provide benchmarking and quality assurance. Intercomparison with other credited research groups of similar systems will be performed as well. The THz detector system needs to be further improved so a portable system can be eventually developed for field application. It is realized that there is a large number of asbestos types to be investigated. The establishment of a complete reference asbestos sample set will continue to be one of the important tasks for the 2nd year of research. The details about the development plan presented in our original proposal will be followed. The final goal is a portable system for field demonstration.

Research will continue to extend the GPDUA to include more realistic in-depth radiological contamination distributions. These will include disk and distributed disks, which are observed shapes after diffusion of contaminants from surface into the porous building materials. Monte Carlo simulations will be used to develop GPDUA, followed by laboratory validations. A commercially available HPGe gamma detector system will be modified with specially designed collimator to accommodate the required counting condition. Dissemination at technical journals/meetings and contacts for preliminary field testing will be pursued aggressively. Again, the detailed research plan presented in the original proposal will be followed. The final goal is also a portable system for field demonstration.

Information Access

1. Naessens, E. P. and Xu, X.G. A Non-Destructive Method To Determine The Depth Of Radionuclides In Materials In-Situ. Health Physics. 77(1):76-88;1999.
2. Chen, Q; Jiang, Z; Sun, F. G.; Zhang, X.-C. Two-Fold Improvement of THz Optoelectronic Generation and Detection. CLEO'99, Baltimore, May, 1999.
3. Jiang, Z.; Sun, F. G.; Chen, Q.; Zhang, X.-C. Electro-Optic Sampling near Zero Optical Transmission Point. CLEO'99, Baltimore, May, 1999.