Environmental Management Science Program 1998 Project Summaries

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1998 Project Summaries

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The Department of Energy Office of Environmental Management (EM), in partnership with the Office of Energy Research (ER), designed, developed, and implemented the Environmental Management Science Program as a basic research effort to fund the scientific and engineering understanding required to solve the most challenging technical problems facing the government's largest, most complex environmental cleanup program.

The intent of the Environmental Management Science Program is to:

- Provide scientific knowledge that will revolutionize technologies and cleanup approaches to significantly reduce future costs, schedules, and risks.

- Bridge the gap between broad fundamental research that has wide-ranging applications such as that performed in the Department's Office of Energy Research and needs-driven applied technology development that is conducted in Environmental Management's Office of Science and Technology.

- Focus the nation's science infrastructure on critical Department of Energy environmental problems.

In an effort to share information regarding basic research efforts being funded by the Environmental Management Science Program and the Environmental Management/Energy Research Pilot Collaborative Research Program (Wolf-Broido Program), this CD includes summaries for each project. These project summaries, available in portable document format (PDF), were prepared in the spring of 1998 by the principal investigators and provide information about their most recent project activities and accomplishments.

Additional information on these research projects and on the Environmental Management Science Program can be found on the Web at http://www.doe.gov/em52/

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Decontamination and Decommissioning

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

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Research Objective

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 and lead along with chromium (as chromate). Anionic 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 groundwater, aqueous waste solutions and mixed waste. Separation and concentration of the target ions will result in a substantial reduction in the volume of material requiring long-term storage.

Research Progress and Implications

This report summarizes work after 8 months of a 3-year project. In the proposed method, a soluble cationic polymer and an anionic ligand are added to the waste stream to be treated. The resulting feed solution is placed in an ultrafiltration (UF) cell that has a membrane with pore sizes sufficiently small to reject the polymer along with any polymer-bound species. Target cations that form anionic complexes with the ligands are electrostatically bound to the polymer and retained during the filtration step. The degree of retention of solute X is expressed as a rejection coefficient, $R_X(\%)$, where

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

$[X]_{per}$ and $[X]_{ret}$ refer the to the concentrations of X in the permeate (filtrate) and retentate (retained) solutions, respectively. In our initial work, dialysis and UF techniques were used to test the effectiveness of carbonate as a ligand for removal of uranyl cation from water.

Equilibrium Dialysis (ED) Studies. Dialysis experiments have been shown to yield the same rejections as observed in ultrafiltration, so most of our results were obtained using this simple technique. The effects of uranyl and carbonate ion concentration, pH, added salt (NaCl), and polymer concentration were investigated using small (10 mL) dialysis cells with cellulose acetate membranes having a molecular weight cutoff of ~6000 Da. Unless otherwise noted, the retentate side of the cell contained 11.65 mM PDADMAC (concentration based on monomer) along with varying concentrations of UO_2^{2+}. Retentate and permeate compartments initially contained equal concentrations of carbonate ($NaHO_3/Na_2CO_3$). A set of baseline studies were carried out to determine the distribution of UO_2^{2+} between permeate and retentate for initial conditions where (i) no carbonate or PDADMAC were present, (ii) PDADMAC, but no carbonate was present, and (iii) carbonate, but no PDADMAC was present. For case (i) the UO_2^{2+} distribution was 1:1, while for case

(ii) electrostatic interaction resulted in net expulsion of ~90% of the uranyl cations into the permeate. In case (iii) a modest rejection of UO_2^{2+} was observed (RUO_2 ~30-60%). The implications of these results are (i) that loses of UO_2^{2+} on the dialysis cell walls or membrane are negligible and (ii) that uranyl cation can be removed after the first separation stage by conversion of the carbonate complexes back to cationic UO_2^{2+}. The result for case (iii) indicates the presence of residual membrane charges, resulting in net rejection of anionic UO_2-carbonate complexes without polymer present. This would tend to enhance the separation process. Based on the results of these preliminary studies, a series of ED experiments were carried out where the UO_2^{2+}, pH, and salt content were varied (10 mM total CO_3). At pH 8.3 ± 0.4, uranyl rejection varied from 99.93 to 99.98% for [UO_2^{2+}] total in the range 0.1-1.0 mM. At pH 10.6 ± 0.1 the rejection values decreased slightly (RUO_2 = 99.48-99.81%) for the same range of initial uranyl concentrations. This corresponds to about 1-4 μM UO_2^{2+} in permeate. The decreased rejection at higher pH may be attributed a shift in the species distribution favoring cationic and monoanionic uranyl complexes {$(UO_2)_x(OH)_z^{2x-z}$, $(UO_2)_2CO_3(OH)_3^-$} relative to the more highly charged $UO_2(CO_3)x^{2-2x}$ species, and to the higher ionic strength of the solutions. ED studies carried out at pH ~ 8.2 in the presence of 0.2 M NaCl gave values of RUO_2 that varied from 33 to 44%. This dramatic decrease in the RUO_2 is attributed to the increased salt concentration which diminishes the polymer-anion interactions. ED studies at low pH showed the feasibility of acid stripping to remove UO_2^{2+} and recover the polymer. At pH 2.3, the [U]per/[U]ret ratio after dialysis was about 1.2. Although the uranyl-carbonate complexes were dissociated, the $[U]_{per}/[U]_{ret}$ ratio was smaller than that found when solutions containing only PDADMAC and UO_2^{2+} were treated by dialysis. This diminution of the ion expulsion effect is most likely due to the increased ionic strength resulting from the presence of ~5 mM HCl and $NaHCO_3$.

Ultrafiltration Studies. The separation behavior in an ultrafiltration (UF) unit was investigated using a 400 mL stirred cell equipped with a 10,000 Da MWCO membrane. Unless noted, feed solution composition was 5 mM PDADMAC, 0.25 mM UO_2^{2+}, 0.25-2.5 mM $NaHCO_3$, pH ~7-8. At pH 7-8, solutions with a [CO_3]:[UO_2] total ratio greater than 4.0 gave RUO_2 = 99.91%. This corresponds to UO_2^{2+} concentrations in the permeate as low as 0.1 micromolar, a reduction of about ~1000-fold in a single separation step. Addition of 0.2 M or 0.5 M NaCl to the feed solution resulted a decrease of the RUO_2 values to ~95% and ~80%, respectively. These results are comparable to the those obtained from ED studies. When the feed solution was adjusted to pH 2.4, uranyl rejection decreased to 70-75%. A similar result (RUO_2 ~80%) was obtained for UF runs using solutions at pH 7-8 containing UO_2^{2+} and PDADMAC, but no $NaHCO_3$. This behavior can be attributed to charge polarization effects that are not observed in ED studies. The combined effects of lowered pH and increased salt concentration may provide a suitable method to remove UO_2^{2+} and recycle the polymer.

Planned Activities

During the next year, we will continue ultrafiltration studies on the UO_2/CO_3 system, with particular attention to the chemical (i.e., pH, salt conc.) and physical (applied pressure, membrane pore size) factors that affect recovery of ligand and polymer. The feasibility of extending the UO_2/CO_3-system to other actinides (e.g., Pu) will be investigated with collaborators at LLNL. The membrane binding properties of ligands selective for other target cations (Th^{4+}, Pu^{4+}, U^{4+}, Pb^{2+}, Sr^{2+}) will be investigated. Ligands to be studied include polycarboxylic acids, disulfonated catechols, and derivatives of polycyclic phenols (calix[N]arenes). ED and UF techniques will be used to evaluate metal ion separation behavior for those ligands that show suitable behavior. Following evaluation of ligands in single cation studies, ligands displaying suitable performance will be tested using mixtures containing other cations and anions (e.g., CrO_4^{2-}).

Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation

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Research Objective

Much of the contaminated concrete from nuclear facilities contains radionuclides only in the near surface region. Removal of the contaminated layer would greatly reduce the volume of waste requiring storage. The objectives of this research are to understand the depth-dependent concentration and chemistry of radionuclide-contaminated concrete surfaces, to determine the mechanism and efficacy of laser ablation in removing contaminated surface layers, and to chemically and physically characterize the captured ablation effluent which would become the stored waste.

Research Progress and Implications

This report summarizes work from the first eight months of a three-year project. Samples consisted of specimens of non-contaminated high density concrete from the Experimental Boiling Water Reactor at Argonne National Laboratory (sectioned into small coupons) and samples cast in the laboratory using Type I Portland cement and either silica, alumina, or sand. Some samples of concrete and cement were doped with Cs-133. Ablation experiments were done with a 1.6 kW pulsed Nd:YAG laser. The beam was delivered via a fiber optic cable, focused to a 0.5 mm spot, and rastered across the surface. The ablated material was collected with a vacuum shroud system and captured on a 0.2 micron filter. Virgin and ablated surfaces were chemically analyzed with laser desorption surface mass spectrometry.

The cement samples melted and vaporized under the influence of the ablation laser. There was no significant difference attributable to the different fillers (i.e. silica and alumina) used. Optical and electron microscopy showed smooth melted surfaces and aerosols composed almost exclusively of hollow spheres less than about 20 microns in diameter. In addition, the aerosols contained a minor fraction (less than about 5% by volume) of grainy agglomerates. Energy dispersive spectroscopy (EDS) showed that the chemical composition of the spheres was essentially identical to the original Portland cement, while the agglomerates were enriched in aluminum. This finding may have significance in light of literature reports showing that Cs ion binds preferentially to alumina and aluminum-rich silica phases [1, 2]. The Cs concentration in our samples was too low to be detected by EDS.

In contrast, ablation of interior sections of high density concrete resulted in a range of ablation mechanisms, from melting and vaporization to disaggregation, depending on whether the laser was focussed on aggregate particles or the cement matrix. The wide range of behavior is attributable to differences in optical absorption and melting points of the various materials present in the sample. The original exterior surface of the high density concrete was simpler than the interior sections, consisting of a 1-2 mm thick layer of Portland cement / sand matrix mostly free of large aggregates due to settling during casting. This material was ablated with the highest efficiency of any sample tested, with ablation rates up to ten times higher than the fresh Portland cement samples cast in our laboratory (0.4-0.8 cubic millimeters/pulse vs. 0.07 cubic millimeters/pulse). The material disaggregated under the influence of the laser, with particles up to 0.5 mm in diameter dislodged. The difference in ablation behavior may be due either to high sand content in the high density concrete or to the expected presence of calcium carbonate in the near-surface region of the sample after many years exposure to air and/or water [3-5].

Cs-doped Portland cement and high density concrete samples were analyzed in ultrahigh vacuum by surface mass spectrometry. Material was vaporized by a pulsed laser focussed to a small (~1 micron) spot on the surface. The desorbed atoms were then ionized by a second laser focussed to a spot above the surface, and analyzed by a time-of-flight mass spectrometer. Laser desorption mass spectrometry and sputtered neutral or secondary ion mass spectrometry are unique in their ability to analyze highly differentiated surfaces such as these with high sensitivity and lateral resolutions of 1 micron or less. The analysis showed Mg, Al, Si, and Ca, representative of the cement matrix, and Na and K, representative of the cement pore water and interstitial surfaces [6, 7]. Cesium was found to be associated with the pore water ions. Preliminary analyses of Portland cement samples doped with known amounts of Cs showed a Cs detection limit in the part per million range. The detection limit is expected to drop as the experimental technique is refined.

A sample of the exterior surface of the aged high density concrete was exposed to an aqueous solution of CsCl and ablated with the high power Nd:YAG laser. Comparison of the virgin and ablated surfaces showed a 30- to 300-fold reduction of Cs after removal of 0.6 to 0.8 mm of material in a single ablation pass.

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Planned Activities

Over the next six to twelve months laser ablation studies will be extended to a more diverse set of samples. Different kinds and amounts of fillers will be used to understand differences in ablation mechanisms. Quantitative surface chemical analyses based on laser desorption, sputtered neutral, or secondary ion mass spectrometry will be developed and used to analyze for cesium and strontium in both the ablated surfaces and captured effluent.

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Advanced Sensing and Control Techniques to Facilitate Semi-Autonomous Decommissioning

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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 and advanced robotics technology.

Research Progress and Implications

This report summarizes work after approximately 1.5 years of a 3-year project.

The autonomous, non-contact creation of a virtual environment from an existing, real environment (virtualization) is an integral part of the workcell functionality. This requires that the virtual world be geometrically correct. To this end, we have encountered severe sensitivity in quadric estimation. As a result, alternative procedures for geometric rendering, iterative correction approaches, new calibration methods and associated hardware, and calibration quality examination software have been developed.

Following geometric rendering, we have focused on improving the color and texture recognition components of the system. In particular, we have moved beyond first-order illumination modeling to include higher order diffuse effects. This allows us to combine the surface geometric information, obtained from the laser projection and surface recognition components of the system, with a stereo camera image.

Low-level controllers for Puma 560 robotic arms were designed and implemented using QNX. The resulting QNX/PC based low-level robot control system is called QRobot. A high-level trajectory generator and application programming interface (API) as well as a new, flexible robot control API was required. Force/torque sensors and interface hardware have been identified and ordered. A simple 3-D OpenGL-based graphical Puma 560 robot simulator was developed and interfaced with ARCL and RCCL to assist in the development of robot motion programs.

Planned Activities

Integration of the 3 subsystems (virtualization, virtual reality and robotics) is anticipated in the Fall of 1998. Following successful completion of this, the first demonstration will be scheduled. In order to expedite the virtualization effort, we are bringing in Dr. Khaled Shaaban from Assiut University as a visiting researcher.

Work continues in efforts to segment the passive image into regions corresponding to individual light stripes, and to establish correspondence between those regions and the projected lines. Complex geometries in unstructured environments yield objects with many parts, limited extent, self-occluding surfaces, and sharp or discontinuous surface boundaries, thus presenting a challenge.

In the development of the new color and texture recognition techniques, it became apparent that an iterative (closed-loop) approach was feasible and likely to provide both further improvements to environment replication and a facility for easily integrating multiple passive camera images into a single environment model. Work is underway on this iterative radiosity. Furthermore, efforts are underway to approximate gaze-dependent rendering.

Near-term robotics objectives include the development of QNX interface software for the force/torque sensors, as well as design and implementation of a low-level force feedback controller for the robots. Tools and tool changer hardware must also be selected and interfaced with the robot control system. A simple disassembly will then be performed using ARCL as the high-level API. Design and implementation of a general-purpose high-level robot control API to replace ARCL is the next major milestone. Furthermore, an operator console must also be designed and interfaced with the system.

Other Access To Information

The following papers have been published as a result of this research effort:

1. “Autonomous Virtualization of Real Environments for Telepresence Applications”, Geist, R., Stinson, T., Schalkoff, R.J., and Gurbuz, S., Presence, Vol. 6, No. 6, December 1997, p. 645-657.
2. “Rendering Inversion in the Automated Construction of Virtual Environments”, Geist, R., Vernon, D., and Schalkoff, R., Proc. 3rd ASCE Specialty Conf. on Robotics for Challenging Environments (ROBOTICS ’98), Albuquerque, New Mexico, April 1998, pp. 85-91.
3. “Geometric Elements of the Direct and Autonomous Virtualization of Quadric Environments”, Schalkoff, R.J., Proceedings Robotics ’98, American Society of Civil Engineers, Albuquerque, NM, April 1998, p.71-77.
4. “QRobot: A Multitasking PC Based Robot Control System”, N. Costescu, M. Loffler, E. Zergeroglu and D. Dawson, IEEE Conference on Control Applications, Trieste, Italy, September 1998.

5. “QMotor 2.0: A PC Based Real-Time Multitasking Graphical Control Environment”, N. Costescu and D. Dawson, IEEE American Control Conference, Philadelphia, Pennsylvania, June 1998.
6. “Tracking Control of Robot Manipulators with Bounded Torque Inputs”, W.E. Dixon, M.S. de Queiroz, F. Zhang, and D.M. Dawson, Proc. of the 6th IASTED International Conference on Robotics and Manufacturing, Banff, Canada, July, 1998, to appear.
7. “Global Adaptive Output Feedback Tracking Control of Robot Manipulators”, F. Zhang, D. Dawson, M. de Queiroz, and W. Dixon, Proc. of the IEEE Conference on Decision and Control, San Diego, CA, Dec. 1997, 3634-3639.

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

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Research Objective

Safe and efficient clean up of hazardous and radioactive waste sites throughout the DOE complex will require extensive use of robots. This research effort focuses on developing Monitoring and Diagnostic (M&D) methods for robots that will provide early detection, isolation, and tracking of impending faults before they result in serious failure. The utility and effectiveness of applying M&D methods to hydraulic robots has never been proven. The present research program is utilizing seeded faults in a laboratory test rig that is representative of an existing hydraulically-powered remediation robot.

Research Progress and Implications

This report summarizes activity conducted in the first 9 months of the project. The research team has analyzed the Rosie Mobile Worksystem as a representative hydraulic robot, developed a test rig for implanted fault testing, developed a test plan and agenda, and established methods for acquiring and analyzing the test data.

The test apparatus consists of a hydraulic power supply system (HPSS) and actuators which are representative of typical components on Rosie. The HPSS includes a 30 kW (40 hp) electric motor drive, capable of providing 75 l/min. at 208 bar (20 gpm at 3000 psi). It is packaged as a single unit with a sump, filters, heat exchanger and circulating pump, accumulator and safety release and pressure control valves. Fluid from this supply flows past another accumulator and through a control valve into the actuator, and then to the system.

The test actuator is a Black Bruin Model 404-080-2111 hydraulic motor. It is a radial piston design and has a maximum power rating of 35 kW (47 hp), a maximum output speed of 185 rpm and can deliver a torque of 2990 Nm at 250 bar (2200 ft-lb. at 3600 psi). In Rosie, this motor directly drives a road wheel and carries the wheel load. For our tests, the motor output shaft is subjected to the loads it would see in service, namely a load equivalent to the nominal weight on the wheel and a torque to resist motion. Radial load is provided by an adapter and a hydraulic jack assembly, and torque is applied by an identical motor, used as a pump, in a “back-to-back” arrangement. The torque loading pump is fed through a separate hydraulic supply consisting of a low-pressure pump, cooler and reservoir. Load will be controlled by means of a throttling valve, with a relief valve to prevent overpressure. The test rig design is complete and fabrication is underway.

A Test Plan has been prepared that describes the test system, the failure issues associated with hydraulically actuated robot subsystems, the applicable portions of Rosie, the methodology used to select and simulate the faults to be implanted, the plans for data acquisition, system control and data reduction, and a test matrix and procedure. The faults to be implanted have been selected and ranked based on importance (criticality and likelihood), ease of implementation and risk to the test

apparatus. The fault list, in ranked order, includes: ruptured pressure supply line, HP pump internal leakage, loss of oil cooling, sticking control valve, control valve open winding, motor encoder feedback loss, internal leak in wheel motor, HPSS pump drive motor fault, broken relief valve spring, loss of accumulator charge, scored HP pump housing, plugged HPSS high side filter, and damaged piston in wheel motor. The actual number of these faults to be implemented will depend on the ultimate complexity of the testing, in order to extract the data needed to characterize each fault reliably.

Methods for data reduction and fault detection include model-based assessments, vibration analysis, temperature and pressure tracking, and a fuzzy expert system. The model-based approach will utilize Analytical Redundancy (AR) to compare signals from the physical system to a real-time simulation of the system. AR is a model-based technique that derives the maximum number of independent tests of the consistency of sensor data with the nominal model and past sensor control input streams. When the system is operational, the parameters of the model will be tuned from nominal values by examination of data streams without implanted faults. Then the data streams from runs with implanted faults will be used to characterize the error signals generated by each type of fault. A fuzzy expert system will be developed to recognize these signals and reject random noise. This will then be tested by running the compiled data reduction system in parallel with the test bed, processing the sensor data in real time, to test and improve its efficiency.

Additional fault detection methods will be implemented and integrated with the expert system. Certain sets of signals such as line pressure, fluid temperature, or tank level, are important fault indicators with minimal processing. The AR techniques should detect many of these faults as well, allowing confirmation of such. Frequency domain vibration analysis of accelerometer data has proven it's worth as a fault detection method, and the existing knowledge of the team in this area will be helpful. Additional methods may be investigated as the project proceeds to add redundancy or cover areas where the planned techniques show inadequate performance.

Planned Activities

The remaining parts for the test rig will be fabricated and the final assembly completed this Summer. Following rig commissioning, an initial series of baseline and implanted fault tests will be conducted. Our plan is to interactively conduct tests, data reduction and diagnostic methodology development so that subsequent tests can be adjusted based on the analysis of data from the initial evaluations.

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

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Mark J. Kurth, University of California at Davis
R. Bryan Miller, University of California at Davis
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: Three classes of ligands are being addressed: (1) acylpyrazolones, (2) polyisoxazoles, and (3) 1,2-aminoalcohols. We are synthesizing representative examples of these three classes of ligands by solution-phase chemistry in order to master the chemistry of these compounds. In the acylpyrazolones, we have prepared over 40 derivatives having variation mainly in the side chain at C-4. One significant finding is that Mitsunobu chemistry allows good regiochemical control for synthesis of O-alkylated systems. Two types of polyisoxazoles have been prepared; one ready for attachment to a water-soluble polymer and another as a monomer for polymerization into a polyacrylamide system. 1,2-Aminoalcohols have been prepared, but this chemistry does not promise to be adaptable to solid phase organic synthesis (SPOS) and therefore we are incorporating this motif as a monomer structural feature into other polymer systems. However, the acylpyrazolones and polyisoxazoles will be studied for use in SPOS and eventual combinatorial application.

(2) Small Ultrafiltration Equipment: To develop a homogeneous synthesis approach a robust, parallel synthesis apparatus which incorporates UF as the mode of separation for ready recovery of polymer/product and removal of excess reagents is under construction. An early prototype was built of Teflonä that incorporated UF membranes at the bottom of cylindrical holes and incorporated vacuum filtration. This unit gave undesirable cross-talk between the individual cylindrical reactors. A second design is in progress that uses centrifugal force for filtration and has individual vessels that can not cross-contaminate.

(3) Rapid Polymer Assaying Techniques: Dried Spot X-Ray Fluorescense: Spotting was on a variety of substrates including polypropylene, Moxtek's AP1 and AP2 films. The AP2 films, which could be heated, exhibited the best spot formation, while a silicone film (Rain-X) helped with spot formation on the polypropylene. Experiments with four surrogate water-soluble polymers at a concentration of 0.5% and 0.1 M $NaNO_3$ resulted in large backgrounds, which obscured analyte signal for the 100 ppb test solution. Further experiments with polymer at 0.1% and no $NaNO_3$ resulted in improved sensitivity. All elements in the test solution were observed in the starting solution, the retentate and filtrate solutions. Qualitatively, the retentate showed greater elemental intensities than the starting solution or the filtrate, indicating a concentration effect by the polymer. The observation of the metals in the filtrate, demonstrated sensitivity approaching 10's of ppb. Increasing counting time increased analyte peak intensities as well as the background. These results indicate the feasibility of using MXRF as a means for screening water-soluble polymer for metal ion binding effectiveness. The next step is to develop a calibration to quantify the metal distribution among the different solutions. Lower polymer concentrations will be studied to further reduce the background and increase sensitivity. Preliminary design plans indicate a good potential for matching the combinatorial reaction vessel with the Moxtek sample holder to maximize sample throughput and minimize confusion during sampling.

Auto-Radiography: Radionuclides (Am, Pu) are prime candidates for radiochemical assay techniques. The polymer/metal ion solutions are placed in a small vessel containing a UF membrane and filtered to near dryness. The sample spot is analyzed using a photographic film, which is placed in close proximity to the radiation source for a time sufficient to

expose the film. In this way a whole series of vessels will be spotted simultaneously using multiple syringe techniques, filtered simultaneously, and exposed to the photographic film simultaneously such that the density of the exposed film will allow determination of the best metal binders. Preliminary tests have involved the use of fixed-sources of radiation, "check" source. These are being used to optimize film types, distance, and exposure times.

(4) Polymer Characterization: Aqueous polymer behavior is in many respects much more difficult to characterize, predict, and evaluate than are organic soluble materials. This is in large part due to the complex nature of water itself, where ionic strength, added ions, pH and temperature all combine to form a very complex environment. Coupling this with the nature of polymeric chelating agents, which are oftentimes ionic, the chemical and physical behavior of such systems can span a wide range. We are employing laser light scattering photometry to evaluate the change in hydrodynamic volume, association of polymers, weight-average molecular weight, and radius of gyration under conditions of varying pH, temperature, ion strength, and added ions to understand the complex conformational aspects of these systems. We are using cadmium NMR to evaluate the metal binding sites on the polymers. We are evaluating the polyamine backbone polymers to baseline the techniques along with some previously functionalized polymers to determine the changes that occur upon functionalization and to develop a database. These capabilities will be transferred to the new polymers as they are discovered in the combinatorial process.

Planned Activities

Some planned activities have been indicated under each individual task. Overall activities will include completion of the synthetic methods development, performing the combinatorial synthesis, testing the polymers on a suite of metals, and characterizing the best candidates

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

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Gayanath W. Fernando, University of Connecticut

Research Objective

The problem being addressed is to establish standards for storage conditions for containers (e.g. stainless steel containers) meant to hold nuclear waste for long periods of time, e.g. fifty years, such as to ensure the integrity of the containers without being excessively conservative, i.e., being unnecessarily costly.

Allowable storage temperature is an important parameter for the standards. Diffusion processes are central to certain processes that initiate corrosion of the containers or that lead to the release of gases increasing pressure that can rupture the container. The scientific goals of this project are: (1) to predict diffusion constants on an ab initio basis, i.e. diffusion distances in specified time at specified temperature, for atomic species from plutonium-based waste materials into storage container materials such as stainless steel or vice versa, (2) to predict the time development at specified temperature of complex diffusion processes in plutonium-based oxide type waste materials in the presence of water vapor such that gases may be released within a container. This predictive ability will help to provide information relevant to setting standards for waste container vessels and storage conditions.

Research Progress and Implications

This project was initiated on September 15, 1997, so that this summary reports progress after about 2/3 of the first year of a three-year project. The diffusion processes of interest will be modeled using kinetic Monte Carlo techniques. The use of this technique in an abinitio-based calculation involves generating atomistic potentials providing the interactions between the atomic species of interest in the solid-state geometry being treated. For systems containing plutonium, we anticipate that the key technical difficulty will be to generate atomistic potentials of sufficient physical accuracy to capture the nature of the interactions involving plutonium in the diffusion processes.

Our initial effort is on the first of the two scientific goals listed above, predicting interfacial diffusion between two metallic systems, one of which is plutonium-based waste, the other of which is a container material such as stainless steel. The necessary modeling involves three steps: (1) ab initio generation of a total energy data base from which atomistic potentials can be extracted, (2) extracting those atomistic potentials in a form tractable for use in the dynamic simulation and sufficiently sophisticated to contain the necessary physics, (3) using these atomistic potentials in a kinetic Monte Carlo calculation to obtain the desired diffusion information.

Initially, we have verified our ability to carry out this procedure on 3d-electron transition metal systems. We have generated our data base by use of our full-potential linear-combination of muffin-tin-orbitals (LMTO) local density approximation (LDA) total energy capabilities; extracted atomistic potentials by use of our previously developed capabilities, already used in such applications as surface relaxation and thermal expansion calculations; and used these potentials in a kinetic Monte Carlo simulation. We have obtained results in excellent agreement with experiment and with other calculations in the literature.

For systems containing plutonium, we anticipate that the enabling steps in the three-step procedure described above are the first and second ones, generating the ab initio data base and extracting the atomistic potentials. We anticipate this because of the well-known limitations of the LDA, in adequately capturing the total energy-density relationship in plutonium. To the best of our knowledge, among all materials to which LDA has been applied, plutonium is the only one for which LDA apparently fails to yield the correct volume within at worst 10% for a structure which is present in the experimentally observed thermal behavior. Typically LDA gives a slightly overbonded prediction of volume, which varies between a volume too low by one or two percent or less at best and eight or nine percent at worst. For plutonium, while a state-of-the-art LDA calculation predicts a volume for the low-temperature monoclinic alpha phase within the usual error bounds, such a calculation for the higher-temperature cubic close packed (fcc) delta phase gives an overbonded volume that is about 30% too low. The legacy wastes of interest are for delta structure materials, so we will have to address this issue. Results, not yet published, from ad hoc refinements of LDA such as LDA+U or LDA-SIC (self interaction corrected) provide a volume for fcc Pu within the usual acceptable error bounds with respect to experiment. These calculations use a different effective potential to treat one-electron dynamics than conventional LDA. This is designed to provide a better treatment of local environment effects for the f-electrons near a Pu nucleus. We do have established LDA+U and LDA-SIC capabilities, and we anticipate having to use such a calculation to generate our data base. We also anticipate the need to use a three-term potential, containing a directional (covalent) term as well as density (embedding) and pair terms. If necessary, we have a detailed working plan for using two-electron dynamics to calculate total energies. We will use such a calculation only if the refinements of LDA fail when our predictions are compared to validation experiments to be carried out at Los Alamos National Laboratory.

As part of our systematic approach to this problem of generating adequate atomistic potentials involving plutonium, we are engaged at present in first calculating the diffusion properties of Pu in a Ni matrix. This is probably the simplest meaningful situation that can be compared to a controlled validation experiment to be conducted at Los Alamos. The calculations are being done for an fcc structure. This initial calculation involves only the density (one-body) and pair terms in the atomistic potential. To obtain the necessary Ni-Pu interactions as well as the purely Pu and Ni effects, we have calculated LDA total energy changes with uniform expansion and fixed volume distortion for a model NiPu intermetallic as well as for pure Pu and Ni. The equilibrium fcc Pu volume is 17%

less than experiment, and the muffin-tin spheres occupy about 65% of the total volume. For the model NiPu intermetallic, the muffin-tin radii were consistently chosen such that the spherically averaged potentials at the muffin-tin radii were approximately equal. The absolute values of the total energy were slightly dependent on the choice of muffin-tin radii, although the equilibrium properties such as volume appear to be stable. We have extracted the atomistic potentials using the technique we have previously used for transition metals. The atomistic potentials for this initial Pu in Ni model situation are now being used to calculate the migration energies and attempt frequencies, and their reliability is being analyzed.

Planned Activities

We will compare to the results for the initial Pu-Ni system to validation experiments at Los Alamos if available. In any case we will systematically proceed to improve the data base and the form used for the atomistic potentials. We will then go on to simulations involving fcc iron containing additives corresponding to stainless steel of interest. We will simulate the diffusion in both directions at the interface between the plutonium-based waste and the metallic container material. We anticipate obtaining meaningful results for the Pu-Ni model system early in the second year and meaningful results for stainless steel interfacing Pu-based waste by the end of the second year. We will then go on to model the oxide-type waste systems.

Other Access To Information

We have established a web page (**http://compmat.phys.wvu.edu/Pu-EMSP.html**) where we will post our progress. We anticipate submitting our first journal publications by the end of the first year or early in the second year.

Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces

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Gary Selwyn, Los Alamos National Laboratory

Research Objective

The object of this research program is to develop an atmospheric-pressure plasma jet for converting transuranic wastes (TRUs) into low-level radioactive wastes (LLWs). This plasma process will be used to efficiently decontaminate a wide range of structures and equipment.

Research Progress and Implications

This report summarizes work after 1 year and 9 months of a 3-year project.

A picture of the atmospheric-pressure plasma jet is shown in Fig. 1. This new plasma source consists of two concentric electrodes through which a mixture of helium and reactive gases flow. The plasma is ignited by applying 13.56 MHz RF power to the inner electrode. The characteristics of this discharge are different from other atmospheric-pressure plasmas, such as transferred arcs, torches, coronas and silent discharges. Shown in Fig. 2 is the current-voltage curve for the plasma jet. Spark breakdown occurs at 0.01 A, and is proceeded by a “normal glow” region, in which the voltage remains constant with increasing current, and an “abnormal glow” region, in which the

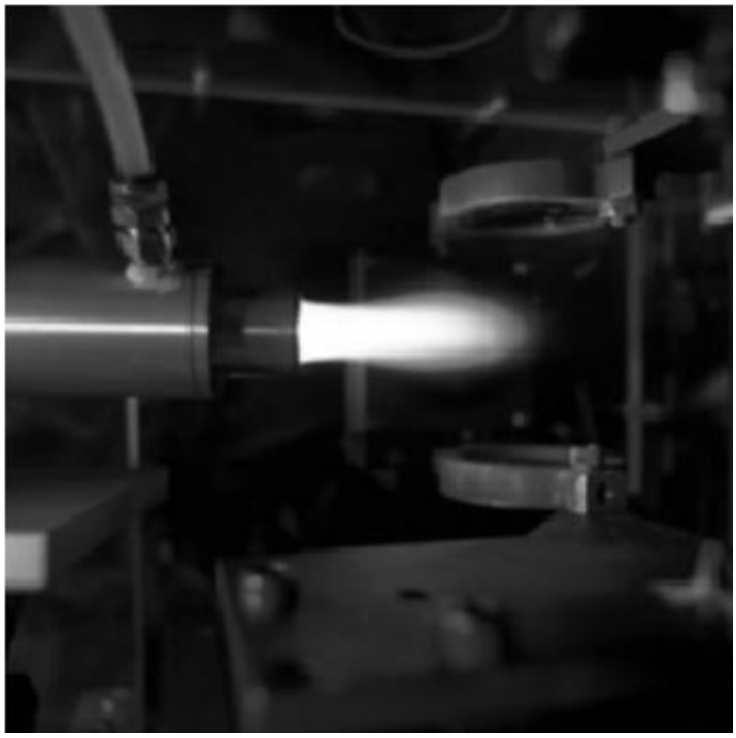

Fig. 1. The atmospheric-pressure plasma jet.

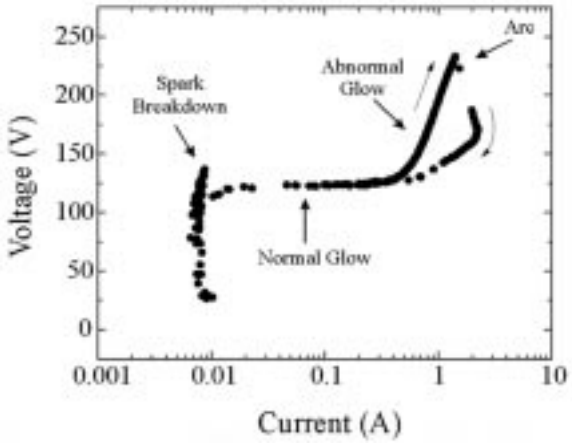

Fig.2. Current-voltage characteristics of the atmospheric pressure plasma jet.

voltage increases rapidly with current. At about 1.0 A and 225 V, the plasma begins to arc. The normal glow region is rarely observed in atmospheric pressure plasmas. They usually proceed directly from spark breakdown to arcing. The trend shown in the figure indicates that the plasma jet is stable over a wide range of operating conditions.

The distribution of reactive species in a plasma jet, containing oxygen and helium, has been characterized by Langmuir probe measurements, optical emission spectroscopy, and ultraviolet absorption spectroscopy. The charged particle density ranges from about $5x10^{11}$ cm^{-3} inside the plasma to $1x10^{10}$ cm^{-3} in the jet exit. The concentration of metastable oxygen molecules ($a^1\Delta_g$ and $b^1\Sigma_g^+$) is estimated to be between 10^{12} to 10^{13} cm^{-3}. By contrast, the ozone concentration increases from about $5x10^{14}$ cm^{-3} inside the plasma to $1x10^{16}$ cm^{-3} in the effluent. The ozone molecules are

produced by the reaction of O atoms with O_2 molecules: $O + O_2 + M \rightarrow O_3 + M$. To generate the amount of ozone observed, the O atom concentration in the plasma must be near $1x10^{16}$ cm^{-3}, or about 10% of the oxygen fed. These results are quite unexpected, because most non-equilibrium, low-temperature plasmas achieve a much lower degree of dissociation.

The etching of actinide metals has been simulated by using tantalum as a surrogate material. Tantalum etching rates of up to 1.2 μm/min are achieved with the plasma jet using a CF_4/O_2/He gas feed. This is 10 times faster than conventional plasma systems, and indicates that our atmospheric-pressure plasma is a promising technology for decontamination of DOE sites.

Finally, the plasma jet has been successfully modified to process larger areas, up to about 1.0 ft^2. Work is underway to increase the process scale further. We are confident that this technology is capable of being adapted for decontamination operations in the field.

Planned Activities

Our research in the third year will include etching of actinide metals (Ur and Pu), further studies of tantalum etching, jet scale-up, and characterization of the chemical constituents in plasmas containing CF_4, O_2, and He gases. A collaboration with the actinide research group at Los Alamos National Laboratory has been established, and a plasma jet will soon be installed in the radioactive material research facility. The other projects are well underway.

Other Access To Information

J.Y. Jeong, S.E. Babayan, V.J. Tu, J. Park, R.F. Hicks, and G.S. Selwyn, Plasma Source Sci. Tech., accepted for publication.
S.E. Babayan, J.Y. Jeong, V.J. Tu, J. Park, G.S. Selwyn, and R.F. Hicks, Plasma Source Sci. Tech., accepted for publication.
Schütze, J.Y. Jeong, S.E. Babayan, J. Park, G.S. Selwyn, and R.F. Hicks, IEEE Transaction in Plasma Sci., accepted for publication.

For more information, visit our web site at: **prosurf.seas.ucla.edu/memc/plasma.html**

In-Situ Spectro-Electrochemical Studies of Radionuclide Contaminated Surface Films on Metals and the Mechanism of their Formation and Dissolution

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Prof. Susan M. Mini, Northern Illinois University

Research Objective

The objective of this research program is to gain a fundamental understanding of the structure, composition, and mechanism of formation of radionuclide-containing surface films on metals that are relevant to the problem of decontamination of piping systems and waste storage tanks at DOE nuclear processing facilities.

Research Progress and Implications

As of May 1998, after about a year and a half of work towards implementing this project, considerable progress has been made in understanding the mechanism and structure of heavy metal ions incorporated into simulated corrosion films of nickel. The nature of iron and chromium oxide films, which are used to model the other components of steels used in piping systems and waste storage

tanks in nuclear facilities, has also been elucidated. The principal techniques used in these investigations consist of coupled electrochemical and “in-situ” synchrotron X-ray absorption spectroscopy, as well as vibrational spectroscopy (infrared and laser Raman).

Electrochemically deposited thin films of nickel hydroxide and nickel oxyhydroxide have been used as models for the host hydrous oxide surface layers initially. Contamination by radionuclides is mimicked by the incorporation of stable isotopes of Sr, Ce, Cs, etc. Co-deposition of Sr with hydrous nickel oxide films resulted in the formation of separate domains of Sr(II) oxide/hydroxide phase without lattice substitution into Ni sites or intercalation into the layered structure.The incorporation of Ce occurs in a similar manner with the exception that only Ce(IV) is found codeposited with NiOOH while Ce(III) and Ce(IV) are formed as co-precipitates of alpha Ni(OH)2. In contrast, Cr is incorporated as Cr(III) into lattice vacancies in Ni(OH)2 and as Cr(VI), in the form of a chromate, in the interlamellar layer of the brucite-type structure. We found that hydrous oxide films of Ce and Cr can be prepared by anodic and cathodic deposition processes. The films can differ in structure and chemical reactivity towards oxygen depending on the composition of the electrolyte solution used. Iron oxide/hydroxide films prepared by anodic deposition were found to have a very similar structure to that of the passivation layer on iron. Thus their study would lead to a better understanding of corrosion and passivation phenomena in metals. The knowledge being gained in this work will be useful in developing rational approaches to the cleanup of contaminated corrosion scales via chemical or electrochemical methods. One would anticipate that more drastic procedures will be needed to remove a contaminant that has been incorporated into a lattice site (e.g. Cr) compared to one which is merely adsorbed on the surface. Our results also have implications in the environmental speciation and remediation of Cr. Moreover, there is great interest in the use of Ce and Cr compounds for corrosion inhibition, as well as in other energy technologies, like water electrolysis.

Results of this research are described in 6 publications to date. They have also been presented at 2 recent scientific meetings, i.e., the Materials Research society Meeting, in San Francisco, in April, and the Electrochemical Society Meeting, in San Diego, CA, in May.

Planned Activities

Future work will involve the use of radioactive isotopes in our studies so as to determine the effect of radiation on the structure, composition, and mechanism of ion incorporation into the corrosion films. The investigation of Cs, U, and Pu will be of particular interest. The structure of sorbed species will be studied. A correlation will be made between the local structure of the incorporated metal ion and its facility for removal via chemical or electrochemical dissolution methods. Finally, we will examine the utility of an “electrochemical brush”, which has been invented in the course of this work, as a practical device for the decontamination of real pipes and storage tanks at DOE facilities.

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

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Prof. Uday Pal, Boston University
M. Eric Schlienger, Sandia National Laboratories
James Stepanek, Sandia National Laboratories

Research Objective

Melt decontamination of radioactive scrap metal could convert a disposal liability into a final product that would reduce the total volume of material necessary for burial and save substantial material costs. The goal of this project is to optimize a melt decontamination process through a basic understanding of the factors which govern the partitioning of various radionuclides between metal, slag, and gas phases. Radionuclides which are captured by a slag phase may be stabilized by promoting the formation of synthetic minerals within a leach resistant matrix. The main focus of this project is the application of electroslag remelting (ESR) toward cleanup of surface contaminated stainless steels.

Research Progress and Implications

This report summarizes work accomplished after 9-months of a 3-year project. Activities are ongoing at Sandia National Laboratories and at Boston University.

At BU, Prof. Uday Pal and his group conduct research to develop a fundamental understanding of thermochemical and electrochemical behaviors of slag/metal/radionuclide surrogate systems. This work combines experimental characterization and thermochemical modeling of these high temperature systems.

First year goals are: 1) to measure and characterize equilibrium partition functions of the surrogate contaminants between the slag and the metal as a function of the temperature and atmosphere. This will include measurements of the rate of approach to equilibrium by determining the partition function as a function of time. The results will be used to model the slag-metal reaction kinetics; and 2) to measure and characterize ionic and electronic conductivities or resistivities of the different slags. The electrical conductivity of the slag will be measured as a function of temperature and oxygen partial pressure.

A laboratory facility has been set up to perform these high temperature measurements; significant effort has gone to development of the necessary crucibles, electrochemical cell configuration, and other experimental techniques for high temperature measurements in the corrosive fluoride-containing molten slags used in ESR. Initial thermochemical modeling began to describe these systems' behaviors.

At Sandia, the goals are to develop models, experimental characterization, and controls for ESR decontamination in a prototype industrial scale furnace. A special vertically-split ESR ingot mold was designed, fabricated, and instrumented with thermocouples. This mold allows detailed examination of slag skin and slag cap structure and chemistry. Process modeling of the ESR furnace has been performed to evaluate the effects of slag chemistry variations on furnace electrical and thermal performance; these will be validated in upcoming experimental melts.

This project is connected with other on-going projects in ESR decontamination through Sandia. A joint effort between Sandia and K-26 in Krasnoyarsk, Russia, funded by the International Proliferation

Prevention Program, is setting up an ESR furnace there to melt surface-contaminated radioactive stainless steel piping. Another project, funded by the Amarillo National Resource Center for Plutonium, supports ESR furnace controls research by Prof. Joe Beaman at the University of Texas in Austin in association with Sandia.

Planned Activities

At Boston University, high temperature slag/surrogate equilibrium measurements and electrical conductivity experiments will begin this summer and continue into 1999. Thermochemical modeling of slag/radionuclide surrogate interactions will continue, utilizing the new experimental data for verification.

At Sandia, over the summer a series of ESR furnace experiments will study effects of slag composition on surrogate pickup by the slag. These fully instrumented melts will measure slag temperatures and furnace thermal performance to help benchmark thermochemical reaction models as well as the ESR furnace melting and solidification model. Solidified slag skin and slag cap structures and compositions will be determined, along with surrogate chemical partitioning between the slag cap and slag skin.

Other Access to Information

Publication and Presentation: Eric Schlienger, Joe Michael, James Van Den Avyle, Davis Melgaard, Greg Shelmidine, “Solidification Sequence as a Means of Containing Radionuclides During Melt Decontamination International Conference on Incineration and Thermal Treatment Technologies, Salt Lake City, May 11-15, 1998

Health/Ecology/Risk

Long-Term Risk from Actinides in the Environment: Modes of Mobility

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Shawki A. Ibrahim, Colorado State University
Thomas Kirchner, New Mexico State University
Jeffrey J. Whicker, Los Alamos National Laboratory
F. Ward Whicker, Colorado State University
Thomas E. Hakonson, Colorado State University

Research Objective

The mobility of actinides in surface soils is a key issue of concern at several DOE facilities in arid and semiarid environments, including Rocky Flats, Hanford, Nevada Test Site, Idaho National Engineering Laboratory, and Los Alamos National Laboratory and the Waste Isolation Pilot Plant (WIPP). Key sources of uncertainty in assessing Pu mobility are the magnitudes of mobility resulting from three modes of transport: (1) wind erosion, (2) water erosion, and (3) vertical migration. Each of these three processes depend on numerous environmental factors and they compete with one another, particularly for actinides in very shallow soils (~ 1 mm). The overall goal of the study is to quantify the mobility of soil actinides from all three modes. Our study is using field measurements, laboratory experiments, and ecological modeling to address these three processes at three DOE facilities where actinide kinetics are of concern: WIPP, Rocky Flats, and Hanford. Wind erosion is being measured with suite of monitoring equipment, water erosion is being studied with rainfall simulation experiments, vertical migration is being studied in controlled laboratory experiments, and the three processes are being integrated using ecological modeling. Estimates for clean up of soil actinides for the extensive tracts of DOE land range to hundreds of billion $ in the U.S. Without studies of these processes, unnecessary clean-up of these areas may waste billions of dollars and cause irreparable ecological damage through the soil removal. Further, the outcomes of litigation against DOE are dependent on quantifying the mobility of actinides in surface soils.

Research Progress and Implications

This report provides a summary of work for the first year of a 3-year project; subcontracts to collaborating institutions (Colorado State University and New Mexico State University) were not in place until late December 1997, and hence this report focuses on the results of the 5 months from January through May 1998. Our major result to date is a review of literature on the potential for using soil concentrations of ^{137}Cs and ^{241}Am as tracers for plutonium in soil. Measurements of ^{239}Pu contamination in the environment are expensive and time consuming, requiring radiochemical analysis and alpha spectroscopy. We evaluated the literature for measurements of ^{137}Cs and ^{241}Am, both of which are more cost-effectively measured by gamma spectrometry, as tracers for Pu in soil. Our results indicate that: significant positive correlation exists between Pu, Cs, and Am in soils and sediments at several locations including Rocky Flats, Los Alamos, and Hanford; atmospheric transport of Pu and Cs from worldwide fallout is essentially the same; the attachment of Pu and Cs to soil particles of various size is very similar; both Pu and Cs movement in the environment correlate well with soil and sediment particle movements; a significant correlation between Pu, Cs, and Am was found in soil as a function of depth, indicating similar vertical migration behavior (most of the activity of these radionuclides is confined to the top 10-20 cm of soil at virtually all locations); most Pu and Cs are strongly absorbed onto clay and organic matter in soils and there is essentially very little leaching of Pu, Am and Cs through soil columns. Based on the above information, we believe

that ^{137}Cs and ^{241}Am are excellent tracers for both ^{239}Pu and soil particle transport processes in clay, mineral bearing and/or organic soils. Therefore, Cs and Am would be good tracers for our proposed water erosion and vertical migration work, at least for both Rocky Flats and Hanford. The correlation between Pu and Cs may not be as strong in sandy soil (e.g. WIPP site), however, we need to examine more data.

Planned Activities

An all-investigators meeting was held at Colorado State University in January, at which time experimental designs were evaluated and tasks were identified and scheduled. Most of the field measurements that we will obtain will be during Summer months when winds are potentially high and soils are dry (expected to lead to higher erosion rates). We therefore decided to conduct field work for FY 1998 at the WIPP site, where logistics are less restrictive. The measurements for the WIPP site will actually be obtained on adjacent BLM land, where the Carlsbad Environmental Monitoring and Research Center is conducting measurements. Measurements will be obtained from Rocky Flats in Summer of 1999 and at Hanford in summer of 2000. Plots for the BLM/WIPP site have been selected and surface characteristics are being measured. An intensive period of field measurement will take place at the site in early June.

Rainfall simulation experiments will be conducted on plots with low and high amounts of vegetation cover. The low cover plots will be disturbed by recent burning, whereas the high cover plots will be undisturbed. The simulator experiments will yield hydrographs and sediment loads for both plot types as a function of ground cover and rainfall intensity. The rainfall simulator has been refurbished, tested, and transported to the field site.

Measurement of transport rates of plutonium contaminated soil through wind erosion will be made and correlated with micrometeorological, soil, and vegetative conditions. These relationships will be investigated with measurements that are averaged over longer periods and short-term, instantaneous, measurements. Longer-time averaged aerosol concentration measurements will be made using passive Bagnold type samplers (for surface creep and saltating soils) and using retrospective and cascade impactor air samplers (for suspended soils). Highly frequent aerosol measurements will be made using up to 26 optical particle counters and sizers. Meteorological conditions will be measured using a 3-dimensional sonic anemometer to measure wind velocity components at rates up to 60 Hz, wind vanes and cup anemometers, air humidity and temperature probes, and rain gauges.

Soil samples for the vertical migration studies will be collected in-tact or in representative layers in early June and returned to Colorado State University for manipulative experiments in soil columns. One set of experiments will focus on the effects of physical factors (wetting/drying cycles and freezing/thawing cycles) on vertical migration; the treatment will be soil columns without rocks, with 25% rocks, and with 75% rocks. A second set of experiments will focus on the effects of biological factors on vertical migration; treatments will include bare soil, vegetated with grass, and grass with introduced earthworms.

Results from all three studies will be integrated using a systems modeling approach. We are currently reviewing a version of the PATHWAY model that was used to evaluate actinide mobility at Rocky Flats. We are identifying processes that will need to be added to the model to compare all three pathways of concern (wind erosion, water erosion, and vertical migration) and evaluating alternative formulations of those processes.

Novel Mass Spectrometry Mutation Screening for Contaminant Impact Analysis

Chung Hsuan (Winston) Chen, Oak Ridge National Laboratory

Research Objective

Our objective is to develop innovative mass spectrometry technology to achieve fast mutation screening from contaminated area and to reveal the linkage between gene mutation and contaminants. In this program, we will try innovative approaches to improve mass resolution and detection efficiency for large DNA ions. Allel specific polymerase chain reaction will be coupled with mass spectrometry for rapid DNA mutation detection. The ultimate goal is to lead to the risk analysis of hazardous wastes to be routinely assessed at DNA level at an affordable cost.

Research Progress and Implications

This report is for the work after 7 months of a 3-year project.

I. Research Approach

Mutations of ras proto-oncogenes are frequently found in animal tumors and certain human cancers. Analysis of mutation spectra of ras genes in human cancers as well as laboratory induced animal tumors has indicated that particular carcinogens may be responsible for specific types of tumors. However, the direct linkage of each individual contaminant to specific mutation is usually not known. For genes which are highly conserve such as ras, the mutation in animal due to the environmental contaminants may have similar effects on human being. In this work, fishes from controlled contaminated area will be used as a model system to test this hypothesis. The data derived from these experiments can provide a critical linkage between the assessment of environmental contamination and the health effects on human subjected to similar exposure. Since the conventional DNA analysis technology is slow and expensive and a large number of DNA samples need to be analyzed for contaminant assessment, we want to develop new mass spectrometric technology for faster, inexpensive and reliable analysis.

The specific approaches of this program includes the following major tasks:

(1) To improve mass resolution by soft acoustic desorption;
(2) To couple with allele specific polymerase chain reaction (PCR) and competitive PCR for quantitative mutation analysis;
(3) Detection of trace mutatnt DNAs by base specific PCR and mass spectrometry;
(4) To identify and clone the exon of ras gene by reverse-transcript polymerase chain reaction (RT-PCR); and
(5) To demonstrate that pollutant-mediated mutations can be used as biological indicators for contaminant impact analysis.

Our major achievements during the past 7 months are in the following:

(1) Facility set-up for DNA extraction, purification and amplification:

Since our laboratory has been primarily involved in laser and mass spectrometry technology development, little facility for DNA sample preparation is available. During the past 7 month, we have purchased and set up the equipments required for DNA extraction from fish sample analysis. We have designed primers for polymerase chain reaction (PCR) amplification of p53 (tumor suppressor gene) and ras (oncogene) from Medaka fish. These primers were used

to amplify the target sequences and will be subject to conventional heteroduplex analysis methods to detect the presence of point mutations.

(2) Detection of point mutation for p53 with synthetic DNAs:

Since p53 mutation is critically important for several different cancers, the capability to detect the mutation of p53 is very valuable for the assessment of the impact of contaminants. We used allele specific PCR and mass spectrometry to successfully detect point mutation with a simulated p53 gene.

(3) Detection of large DNA fragments from enzyme digestion by matrix-assisted laser desorption/ ionization:

Rapid measurements of DNA polymorphism are very valuable for mutation identification. A few DNA samples from microbials have been digested with various enzymes. Laser and mass spectrometry were used to measure these enzyme digested products. These samples were also measured by gel electrophoresis. The results from two different approaches agree each other.

(4) Detection of DNA fragments larger than 1000 nucleotides:

By using new matrices and DNA purification processes, we succeeded in using matrix-assisted laser desorption/ionization for detection of DNA fragments with the size of 1500 base pairs. To our knowledge, it is the largest DNA fragments to be detected by a time-of-flight mass spectrometer. It indicates that mass spectrometer can possibly be used to separate large DNA fragments.

Planned Activities

The following tasks will be pursued in the future.

(1) Design, install, and test the new detection scheme with laser induced multiphoton ionization of large DNA fragments (10/31/98);
(2) Design, install, and test DNA desorption by acoustic shaking (12/31/98);
(3) Develop quantitative PCR mass spectrometry for quantitative DNA measurements (05/31/99);
(4) Detection of trace gene mutation by ASPCR and mass spectrometry (10/31/99);
(5) Identify and clone ras gene of fish (03/31/2000); and
(6) To demonstrate that mutation screening of fish can be used to assess contaminants impact to human health (09/30/2000).

Comparison of the Bioavailability of Elemental Waste Laden Soils Using "In Vivo" and "In Vitro" Analytical Methodology and Refinement of Exposure/Dose Models

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Brian Buckley, Ph.D., Rutgers, The State University of New Jersey

Research Objective

Our hypotheses are: 1) the more closely the synthetic, in vitro, extractant mimics the extraction properties of the human digestive bio-fluids, the more accurate will be the estimate of an internal dose; 2) performance can be evaluated by in vivo studies with a rat model and quantitative examination of a mass balance, calculation and dose estimates from model simulations for the in vitro and in vivo system; and 3) the concentration of the elements Pb, Cd, Cr and selected Radionuclides present in the bioavailable fraction obtained with a synthetic extraction system will be a better indicator of contaminant ingestion from a contaminated soil because it represents the portion of the mass which can yield exposure, uptake and then the internal dose to an individual.

Research Progress and Implications

As of April 15, 1998, we have made significant progress in the development of a unified approach to the examination of bioavailability and bioaccessibility of elemental contamination of soils for the ingestion route of exposure. This includes the initial characterization of the soil, "in vitro" measurements of bioaccessibility, and "in vivo" measurements of bioavailability. We have identified the basic chemical and microbiological characteristics of waste laden soils. These have been used to prioritize the soils for potential mobility of the trace elements present in the soil. Subsequently we have employed a mass balance technique, which for the first time tracked the movement and distribution of elements through an "in vitro" or "in vivo" experimental protocol to define the bioaccessible and the bioavailable fractions of digested soil. The basic mass balance equation for the "in vitro" system is:

$$MT = MSGJ + MIJ + MR.$$

where MT is the total mass extractable by a specific method, MSGJ, is the mass extracted by the saliva and the gastric juices, MIJ is the mass extracted by the intestinal fluid, and MR is the unextractable portion of the initial mass. The above is based upon the use of a synthetic digestive bio-fluids model that includes the saliva, gastric juices, and intestinal fluids. The system has been devised to sequentially extract elements from soil by starting with an extraction by the saliva and carrying the entire mixture to the subsequent bio-fluids for further extraction. The residence time of the soil in each extractant and the liquid to mass ratio in the gastric juices are based upon typical values known for the human digestive system. Experiments were conducted to examine the sensitivity of the extractions to changes in these major variables. The results indicated the lack of significant extraction after 2 h of residence in gastric fluid. The range of variation of the liquid to mass ratio was element dependent over the interval 100:1 and 5000:1. The final values used for the extraction protocol were: 2 h residence time , and a ratio of 1000:1. Details of the chemical composition of the extraction protocol are found in Hamel, 1998.

The mass balance technique was tested in the “in vitro” system for a number of soils. One of major interest was a residential soil from Bunker Hill, ID which was impacted by mining wastes. It was used because of experimental evidence of human bioavailability of lead in the soil based on an adult feeding study conducted at Columbia University. We examined the particle size fraction of <125 μm diameter soil which contained a total Pb concentration of 2900 μg/g. The results of our experiments on soil found the total bioaccessible fraction for lead in the synthetic digestive fuilds to be 70%+/-11%. The human study found the bioavailable fraction, as indicated only by the blood lead levels, to be at least 26%+/-8.1%.

A non-radioactive soil from Savannah River have been subjected to the “in vitro” ; mass balance using the same protocol as above. The Pb level was the only one with values of any interest, but was less that 50 μg/g. In any case, the bioaccessibility of the Pb in the soil was approximately 40%. In this case the analyses were completed on the size fractions <75 μm and < 250 μm in diameter, and the bioaccessibility was the same for both fractions. Based upon other studies, the results are consistent with an un-contaminated background soil.

Another major aspect of the project is the “in vivo”; studies being conducted on a Sprague-Dawley rat animal model with some of the same soils used for the “in vitro” studies. In this case we feed 15 rats contaminated soil, and sacrificed them at 3-4 days post feeding with the soil in their food. The internal organs, blood and feces were subsequently subjected to extraction and analysis for the elements examined in the “in vitro” system. The approach was again designed to provide a mass balance of the elements as they distributed throughout the body, and then provide an estimate of the bioavailable fraction of the element in the soil.

The results for our first experiment using a soil contaminated with As, Cr, Pb collected in Jersey City, NJ. The relationship between what is known as the bioaccessible and the bioavailable fractions was dependent upon the element. The As, Cr, and Pb were 65%, 7.1% and 62% bioaccessible, respectively. The amount of bioavailable As, Cr, and Pb was 44%, 0.2%, and 2%, respectively. Even with the large variations between elements the results were physiologically plausible because all of the material that is released into the digestive (bioaccessible) will not be transported across the stomach or intestinal lining into the blood and other tissues (bioavailable).

Thus far part of our research has focused on how to best develop an “in vitro”; system which minimizes the number of steps used to obtain data on bioaccessibility. For that reason we are now optimizing the system for the analysis of only the bioinaccessible portion of the mass. This will allow us to add more of the minor components of the various biological fluids to the extraction protocols while reducing the number and complexity of the analyses. Initial results suggest that the bioaccessiblity moves closer the bioavailable fraction with the addition of some key organic compounds.

Planned Activities

We have recently developed 1) a self-contained sieving system for the fractionation of soil that contains radionuclides by particle size, and 2) protocols for the extraction of the Radionuclides with the “in vitro” system. These will now be applied to a radionuclide laden soil from Savannah River. Parallel tests will be completed with the “in vivo” system. We are in the process of analyzing the data obtained for an “in vivo” and “in vitro” mass balance of a standard NIST soil. The results will be valuable for future inter-comparisons of our system with other approaches to bioavailability. Future activities will include continued “in vitro” studies in association with Consortium for Risk Evaluation with Stakeholder Participation (CRESP).

Other Access To Information

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Improved Radiation Dosimetry/Risk Estimates to Facilitate Environmental Management of Plutonium Contaminated Sites

Bobby R. Scott, Lovelace Biomedical &Environmental Research Institute

Research Objective

The objective of this research is to evaluate distributions of possible alpha radiation doses to the lung, bone, and liver and associated health-risk distributions for plutonium (Pu) inhalation-exposure scenarios relevant to environmental management of PuO_2-contaminated sites. Currently available dosimetry/risk models do not apply to exposure scenarios where, at most, a small number of highly radioactive PuO_2 particles are inhaled (stochastic exposure [SE] paradigm). For the SE paradigm, risk distributions are more relevant than point estimates of risk. The focus of the research is on the SE paradigm and on high specific activity, alpha-emitting (HSA-aE) particles such as $^{238}PuO_2$. The scientific goal is to develop a stochastic respiratory tract dosimetry/risk computer model for evaluating the desired absorbed dose distributions and associated health-risk distributions, for Department of Energy (DOE) workers and members of the public.

Research Progress and Implications

This report summarizes results after 1 year of a 2-year project. The key research achievements and their implications are as follows:

The respiratory tract dosimetry computer program, LungMod, developed at our Institute for the National Council on Radiation Protection and Measurements was updated to a 32-bit version applicable to both monodisperse and polydisperse aerosols. The program is being used to evaluate Pu-particle regional deposition efficiencies throughout the respiratory tract.

A Monte Carlo (MC)-based computer program (preliminary) was developed for calculating the distribution of radioactivity intake via inhalation of $^{238}PuO_2$ by male adults. The program was applied to a scenario where one person in 100 is expected to have a particle presented for inhalation. The intake distribution obtained was used for an upper-bound, intake distribution for members of the public (infants, children, teenagers, adults) who inhale dust contaminated with $^{238}PuO_2$, when up to one person in 100 inhales one or more contaminated dust particles.

Single-particle radioactivity intake distributions (conditional on particle deposition) were developed for HSA-aE, $^{238}PuO_2$ aerosols for the SE paradigm, for male adults. Evaluations were conducted for a lognormal size distribution with activity median aerodynamic diameter of 5 mm and geometric standard deviation of 2.5.

Single-particle intake distributions were convoluted to obtain multiple-particle intake distributions for up to 10 particles. For $^{238}PuO_2$, radioactivity intake for 10 deposited particles in the respiratory tract spanned a wide range. The 2.5%, 50%, and 97.5% (percentiles) of the intake distribution were 0.28 kBq, 2 kBq, and 7.5 kBq, respectively. Corresponding values for $^{239}PuO_2$ can be obtained by dividing the indicated values for $^{238}PuO_2$ by 280.

The stochastic geometry model of Werner Hofmann and colleagues was acquired and will be used to evaluate variability in deposition of particles in the respiratory tract. The model allows the lung morphometry to vary in a stochastic manner, based on measured distributions.

We are updating information on current knowledge about cancer induction by alpha particles. A key issue being addressed relates to the validity of the linear, no-threshold (LNT) model for cancer induction. Data we acquired, based on a recent case-control analysis of Mayak workers by Russian scientists, indicate that a sizable threshold may exist for alpha radiation-induced lung cancer. Evidence

for thresholds for radiation-induced cancer at other sites in the body is also growing and has cost-saving implications for cleanup of Pu-contaminated, DOE sites.

We are maintaining a database on worker exposure to Pu.

The key implications of the research conducted for the SE paradigm are as follows: (1) single-particle intake should predominate when less than 1 in each 100 members of the public are presented a PuO_2 particle for inhalation; (2) the intake of a single HSA-aE, PuO_2 particle could exceed the annual limit for worker exposure; (3) widely varying amounts of radioactivity can be deposited in the respiratory tract, even for a fixed number of HSA-aE, PuO_2 particles inhaled; (4) use of point estimates of dose and average risk based on the LNT health-risk model could lead to wasting dollars on excessive cleanup of Pu-contaminated sites.

Planned Activities

Over the next year we will: (1) place a database developed in this project on Pu exposure of workers onto the World Wide Web; (2) complete research on characterizing source terms for potential DOE-worker and public exposures; (3) apply the stochastic geometry model of Hofmann and colleagues in variability evaluations related to particle deposition in the respiratory tract; (4) initiate and conclude research on characterizing absorbed radiation dose distribution for key organs, for the SE paradigm; (5) characterize lung, bone, and liver cancer risk distributions for plausible DOE-worker and public-exposure scenarios for the SE paradigm; and (6) deliver a stochastic respiratory tract dosimetry/risk computer model applicable to inhalation exposure to Pu aerosols for the SE paradigm.

Other Access To Information

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Measurements of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational & Environmental Exposure & Risk at Fernald Feed Materials Production Center

Naomi H. Harley, New York University School of Medicine

Research Objective

1. To develop an accurate personal radon/thoron monitor to quantitate exposure during remediation. This personal monitor is a miniaturization and modification of our area ^{222}Rn monitor that has proven accuracy and precision.

2. To develop a personal aerosol particle size sampler, based on the principles of the novel sampler we have developed. The sampler measures not only ^{222}Rn decay product aerosol size but long lived nuclides. There are, as yet, no size distribution data on the aerosol particle size distribution of these nuclides during remediation, yet the aerosol particle size is the major determinant of lung dose.

3. To develop the sequential radiochemistry necessary to measure any environmental sample for $^{228,230,232}Th$, $^{226,228}Ra$, $^{234,235,238}U$ and ^{210}Pb. To utilize the radiochemistry to accurately trace and delineate these nuclides in the environment. To obtain historic and present radiochemical data to understand the need for supplemental soil/water etc. measurements.

Research Progress and Implications

1. As of June 1998, we have designed the personal radon/thoron monitor and it is being fabricated at a commercial molding facility. It contains 3 separate entry ports for 3 alpha track films, each port is gas sealed and contains a specific gas entry diffusion barrier. The radon versus thoron gas concentration is obtained by signal differencing, using different diffusion barriers for radon and thoron gas. The alpha track film area is 1 cm^2 and has only few background tracks on the pristine film. The detection limit for either radon and thoron is 3 pCi/L day. The exterior shape is triangular and the overall dimensions small enough so that it can be worn on a lapel without worker interference.

This personal monitor can be used either as an area monitor or a personal monitor.

2. As of June 1998, we have performed research using a personal aerosol particle sampler, modified to measure 3 particle size regions. The sampler is a lapel monitor using a belt pump. The original commercial sampler used an impactor entry to eliminate particles greater than 2.5 micrometers. Particles less than 2.5 micrometers are measured on the backup filter. Our modification uses ZnS alpha phosphor on the impactor stage, followed by several 500 mesh wire screens, then followed by the backup filter. This design permits actual measurement of the alpha particle radioactivity on particles greater than 10 micrometers, the screens permit the measurement of ultrafine and fine particles and the backup filter 0.05 to 2.5 micrometers size particles. These multiple stage alpha particle radioactivity measurements permit the use of our size deconvolution program to determine the aerosol particle distribution with high accuracy.

To measure the alpha particle radioactivity on filters, screens, etc. we use our high efficiency (50%), low background (5 count per day) alpha counters that were designed in house.

We have tested the modified aerosol particle size sampler in the basement of a suburban home. The alpha particle radioactivity measured on the screens and filters is the natural airborne radionuclide ^{212}Pb present from the decay of ^{220}Rn (thoron). These tests show that even at normal environmental low activity concentrations, it is possible to measure the size distribution accurately. During the next year we plan to fully calibrate the monitor in the NYU Test Aerosol Facility, and further modify the input impactor stage to permit a smaller size cutoff. This permits more detailed information in the 0.05 to 0.2 micrometer size range. These very small aerosol particles deposit efficiently in the bronchial airways, and in general deliver the major radiation dose to the airways in any exposure situation.

Both the personal radon/thoron monitor and the personal aerosl size sampler can be adapted for use at any DOE facility.

Planned Activities

We have established our first visit to the plant for mid June 1998. At this time all of the DOE and FERMCO individuals in charge have agreed to guide us in the research, and explain the work that has been accomplished. They plan to discuss and set up the new work areas and environmental locations that are of interest to monitor for radon thoron concentrations and aerosol particle size, using the new instruments described above.

Also during this visit the USDOE consultant on our project (Dr. Isabel Fisenne, Environmental Measurements Laboratory) will accompany on this field trip and will be given access to the existing environmental radiochemical sampling and analysis data. She will assist in the QA/QC during remediation and locate the areas where research and additional radiochemical sampling will assist the overall Fernald project.

During the next year we plan at least 2 data gathering field trips to begin actual concentration measurements using the newly designed personal monitor, and aerosol particle sampling with the personal aerosol particle size sampler. These data will provide background information so that we can plan for best sampling times and locations.

Other Access To Information

Information concerning radon measurements using the original radon monitor design may be viewed at **http://charlotte.med.nyu.edu/faculty/harleyN.html**

Mechanism Involved in Trichloroethylene-Induced Liver Cancer: Importance to Environmental Cleanup

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Research Objective

The objective of this project is to develop critical data for changing risk-based clean-up standards for trichloroethylene (TCE). The project is organized around two interrelated tasks:

Task 1 addresses the tumorigenic and dosimetry issues for the metabolites of TCE that produce liver cancer in mice, dichloroacetate (DCA) and trichloroacetate (TCA). Early work had suggested that TCA was primarily responsible for TCE-induced liver tumors, but several, more mechanistic observations suggest that DCA may play a prominent role. This task is aimed at determining the basis for the selection hypothesis and seeks to prove that this mode of action is responsible for TCE-induced tumors. This project will supply the basic dose-response data from which low-dose extrapolations would be made.

Task 2 seeks specific evidence that TCA and DCA are capable of promoting the growth of spontaneously initiated cells from mouse liver, in vitro. The data provide the clearest evidence that both metabolites act by a mechanism of selection rather than mutation. These data are necessary to select between a linear (i.e. no threshold) and non-linear low-dose extrapolation model.

Research Progress and Implications

As of May of 1998, this research has identified two plausible modes of action by which TCE produces liver tumors in mice. These modes of action do not require the compounds to be mutagenic. The bulk of the experimental evidence suggests that neither TCE nor the two hepatocarcinogenic metabolites of TCE are mutagenic. The results from our colony formation assay clearly establish that both of these metabolites cause colony growth from initiated cells that occur spontaneously in the liver of $B_6C_3F_1$ mice, although the phenotypes of the colonies differ in the same manner as tumors differ, in vivo. In the case of DCA, a second mechanism may occur at a lower dose involving the release of insulin. This observation is timely as it was recently reported that occupational exposures to trichloroethylene results in 2 to 4-fold elevations in serum insulin concentrations, as well. The increases in insulin have not been shown responsible for the induction of liver tumors. Therefore, this problem is a subject of a proposal to the Office of Biological and Environmental Research Low-Dose Initiative. However, even if this is demonstrated to be the most sensitive mechanism for liver tumor induction, it is unlikely to contribute to induction of cancer at lower doses, since this involves modification of normal endocrine function. As doses are decreased to levels that do not induce increase in serum insulin level, there should be no risk from this metabolite either. Therefore, there is clearly a rational basis for considering a margin of exposure for low dose extrapolation of liver cancer risks for TCE.

Planned Activities

There are technical questions that still arise from whether TCA or DCA is primarily responsible for the induction of liver cancer. If TCA could be shown solely responsible for the tumors, it would simplify the argument for low dose extrapolation. Our current pharmacokinetic data does not allow us to conclude that effective concentrations DCA are not formed from TCE because the effective carcinogenic concentrations in blood at the limit of detection. We will pursue this further during the final phases of this project. Nevertheless, the demonstration that DCA is also acting by a tumor promoting mechanism will still provide a basis for using a threshold or margin of exposure approach for estimating cancer risk.

Beyond completing current experiments and analysis of data that has already been generated in the project, our research over the remaining period of the project is to obtain good dose-response data on insulin- releasing properties of DCA and make certain that TCA does not also produce the same effect. If these data prove that the effect is specific for DCA, we will evaluate serum insulin concentrations in animals being chronically administered TCE. If serum insulin is increased in these animals, we should be able to use serum insulin levels as a surrogate for effective doses of DCA derived from TCE. In addition, we are pursuing further the possibility that the key step in TCA-induced carcinogenicity may be attributed to the induction of phosphotidylinositol-3-kinase activity.

A member of our research team (RJB) is preparing the final draft on the mode of action paper being used by the Environmental Protection Agency as a test case for their new Proposed Cancer Risk Assessment Guidelines. The arguments put forward above have been generally accepted by the Agency and will form the basis for their decision. Since kidney tumors in rats are also produced with TCE, the impact of this work will be to change the potency estimate from that derived on liver tumor induction in the mouse to kidney tumor induction in mice. This should decrease the estimated risk per unit dose by approximately 10-fold. Informal discussions have been conducted with the Office of Water of the EPA to determine if that office is going to be responsive to any new recommendations from the National Center for Environmental Assessment related to low-dose estimates of cancer risk associated with trichloroethylene. If the new guidelines are determined appropriate for liver tumor induction by TCE, they do intend to determine whether the drinking water MCL should be revised.

Other Access To Information

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Environmental Analysis of Endocrine Disrupting Effects from Hydrocarbon Contaminants in the Ecosystem

John McLachlan, Tulane University

Research Objective

The objective of this project is to determine how environmental contaminants, namely hydrocarbons, can act as hormones or anti-hormones (i.e., environmental hormones) in different species present in aquatic ecosystems. Species of particular focus are those which can serve as sentinel species (e.g., amphibians) and, thus, provide early warning signals for more widespread impacts on an ecosystem and its wildlife and human inhabitants.

Research Progress and Implications

This reports the progress of 1.5 years of a three-year grant awarded to the Tulane/Xavier Center for Bioenvironmental Research (CBR).

A growing body of evidence suggests that chemicals in the environment can disrupt the endocrine system of animals (i.e., wildlife and humans) and adversely impact the development of these species. Because of the multitude of known endocrine-disrupting chemicals and the numerous industrial and government sectors producing these chemicals, almost every federal agency has initiated research on the endocrine effects of chemicals relevant to their operations. This study represents the Department of Energy (DOE) Basic Energy Sciences' only research on the impacts of endocrine-disrupting chemicals. The activities employed by this project to determine these impacts include development of biotechnology screens (in vitro), animal screens (in vivo), and other analyses of aquatic ecosystem biomarkers of exposure. The results from this study can elucidate how chemicals in the environment, including those from DOE activities, can signal (and alter) the development of a number of species in aquatic ecosystems. These signals can have detrimental impacts not only on an organismal level, but also on community, population, and entire ecosystem levels, including humans.

Biotechnology Screening System

Three biotechnology screens have been developed and tested through this grant: 1) the Yeast Expression System (YES), 2) an *in vitro* screen for thyroid hormone disruption, and 3) an *in vitro* screen for the Arthropod ecdysone receptor. These screens allow us to test the ability of PAHs and other environmental hormones on hormone receptors of humans, amphibians, and invertebrates (e.g., shrimp). Development of all of these screens is completed and all have demonstrated success in identifying numerous compounds, including PAHs, which interact with these important receptors.

Animal Screening

Three animal screen studies have been funded through this grant and include the effects of environmental hormones on: 1) the African clawed frog (*Xenopus laevis*), 2) the leopard frog (*Rana pipiens*), and grass shrimp (*Palaeomonetes* spp.). Frogs were chosen as species of concern since unusual frequencies of frogs with morphological abnormalities have been observed recently in western North America; environmental hormones are capable of disrupting reproductive physiology in amphibians; amphibians are often the most susceptible species for adverse environmental impacts (and, thus, can serve as sentinel species for ecosystem inhabitants); and many are threatened and endangered. Grass shrimp were chosen as species of concern because of their economic and ecological value and because of the many industrial impacts on their aquatic habitats.

Since frog metamorphosis is primarily controlled by thyroid hormones, we used metamorphosis as a model for environmental hormone interaction with the thyroid axis. We exposed premetamorphic tadpoles of the African clawed and leopard frogs to a variety environmental hormones and measured growth and rate of metamorphosis. For both frog species, metamorphosis was affected (either delaying or accelerating metamorphosis) by these environmental chemicals. For the African clawed frog, in particular, biomarker analyses suggest that the endocrine neuroimmune systems could be adversely impacted by various hydrocarbons and organometals.

The impact of PAH contamination on grass shrimp was investigated in a contaminated bayou and in the lab. Grass shrimp caught in the bayou showed a contaminant-gradient increase in heat shock protein 63 and cytochrome P450 1A (as measured by ECOD metabolism). Grass shrimp exposed to contaminated sediment in the laboratory showed a trend for elevated ECOD metabolism, however individual variation was too large for statistical significance. Heat shock proteins were also not significantly elevated in laboratory exposed shrimp. This lack of significant increase in these two biomarkers could be due to the short exposure regime.

Planned Activities

During the remainder of this grant period (approximately 1.5 years), the investigators intend to continue development of animal screen and biomarker analyses for environmental hormones. The shrimp screening has recently been initiated and will, therefore, continue for at least one more year. Animal screens with fish will possibly initiate in Summer or Fall, 1998.

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Environmentally-induced Malignancies: An In Vivo Model to Evaluate the Health Impact of Chemicals in Mixed Waste

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Research Objective

Increased risk of malignancy following exposure to genotoxic agents in the environment is a major public concern. Exposure to radiation, benzene, and organic solvents is associated with an increased risk of leukemia; however the mechanism of leukemogenesis is unknown. We postulate that chemical(s) that increase the rate of genomic instability and induce hematotoxicity will promote accumulation of genetically-damaged hematopoietic stem cells (hsc), and thus contribute towards development of environmentally-induced hematologic malignancy. We will use molecular and cellular approaches to establish the relationship between hematoxicity, genomic instability and production of genetically aberrant hsc and progeny in mice exposed to radiation, benzene and trichloroethylene (TCE). The goals of this project are to

1) Determine whether recruitment of hsc into cycle by agents that induce hematotoxicity (i.e., pancytopenia, anemia) facilitates fixation of genetic damage in hsc exposed to environmental genotoxins in vivo.
2) Determine whether environmental genotoxins with leukemogenic potential disrupt hsc genomic integrity by inactivating cell cycle checkpoints.
3) Determine whether low dose exposures to agents that induce chronic pancytopenia/anemia and/or cyclic hemopoiesis increase fixation of genetic damage in hsc.

Increased understanding of the relationship between genotoxicity, hematotoxicity and genomic instability will a) lend insight into mechanisms underlying environmental-induction of leukemic progression, b) facilitate development of a rationale to identify chemical combinations which synergize to increase or decrease leukemogenic potential, and c) provide opportunities to optimize approaches for biomonitoring and risk assessment.

Research Progress and Implications

This report summarizes work after 1.5 year of a 3 year project. Accomplishments to-date include demonstration that the cycling status of hemopoietic stem cells at the time of genotoxin exposure alters the frequency and persistence of genetically damaged hemopoietic stem cells and associated progeny (Aim #1), development of assays to measure genomic instability in hemopoietic stem cells and associated progenitors (Aim #2) and quantification of genomically aberrant hsc and progeny

following radiation, benzene and TCE exposures (Aim #2). Mice with varying susceptibility to leukemogenesis have been exposed to combinations of radiation, benzene and TCE to allow assessment of the cellular and genomic perturbations associated with leukemogenesis.

Hsc are quiescent cells in the marrow responsible for lifetime maintenance of blood cell production. Hsc can be activated and recruited into cycle by regulatory cytokines or reduced numbers of circulating cells. Genetic damage in quiescent hsc may be more readily repaired, thus preventing propagation of genetically damaged progeny. We postulated that recruitment of hsc into cycle by agents that induce hematotoxicity (i.e., pancytopenia, anemia) will increase the frequency of hsc with genetic alterations and consequently result in elevated levels of genetically aberrant hematopoietic cells that persist during lifetime hematopoiesis (Aim #1). We tested this hypothesis by recruiting stem cells into cycle using 5-fluorouracil prior to radiation and benzene exposure, and then measured the frequency of genetically aberrant hsc and circulating cells 6, 12 and 15 months later. Our data demonstrate that radiation and benzene induce genomic changes (translocations and aneusomies) that persist for extended time periods after exposure. However, at 12-15 months post exposure, hsc that were in S-phase at the time of genotoxin exposure generated fewer genetically aberrant progeny than hsc that were not replicating DNA. The frequency of aberrant cells appears to be dependent upon the degree of cytopenia. We now postulate that persistent pancytopenia places a high demand on hsc replication and differentiation, and that differentiation of these cells to replace hematopoiesis results in eventual (i.e. by 6-12 months) elimination of the genetically damaged cells. New experiments to recruit hsc into cycle in the absence of cytotoxicity are underway to confirm this hypothesis.

These data have major implication for risk assessment. They demonstrate that persistence of genetically damaged blood cells is highly dependent upon the cycling status of hsc at the time of exposure. Thus, exposure to mixtures of chemicals and/or radiation that affect the cycling status of hsc are likely to have different long term health effects than single agent exposures. Importantly, in some situations, particularly those associated with hematotoxicity, high dose exposures may result in fewer genetically damaged cells than low dose exposures. The dose-response relationship of this phenomena needs further exploration.

Development of malignancy is associated with accumulation of multiple genetic alterations that result in dysregulated cell growth and differentiation. It has been suggested that multiple genomic aberrations arise because a cell becomes genomically unstable. Thus, we postulated that exposures to mixtures of genotoxins that induce genomic instability will result in accumulation of genetically aberrant cells, and in some cases cell cycle checkpoint inactivation (Aim #2). Conventional assays of genomic instability rely solely on in vitro exposures and have been applied primarily to epithelial cells. However, regulation of hematopoiesis is dependent upon complex interactions between hemopoietic cells and their microenvironment, thus, we desired to measure genomic instability after exposures in vivo. We have developed a two-step assay that measures the ability of hematopoietic stem cells to amplify regions of their genome and proliferate under selective pressure. Thus, induction of genomic instability in hsc in vivo can now be assessed using selective pressure cell culture conditions. We have verified that this assay is capable of detecting hsc with checkpoint inactivation that have lost one or both alleles of p53, a cell cycle checkpoint regulator. Evaluation of genomic instability in hsc induced by combinations of radiation, benzene, and TCE exposures in vivo are in progress and represent the first analyses of genomic instability in a rare cell subpopulation involved in leukemic progression.

The development of leukemia is a time-dependent process that requires not only the induction of genomic alterations in cells at risk of clonal expansion, but also the selective propagation of cells with genomic aberrations. We postulated exposure to low doses of chemicals and radiation in complex mixtures would increase the risk of leukemogenesis, and that the development of leukemia would be associated with genomic instability, hsc recruitment and accumulation of genetically aberrant cells (Aim #3). These studies are in the early stages. Mice with different genetic susceptibilities to development of leukemia have been exposed to radiation, benzene and TCE. Leukemia is expected to develop at 7-9 months post exposure. Thus, we are in the process of characterizing the early cellular and genetic changes that occur in hsc in animals exposed to these combinations of genotoxins.

Planned Activities

During the forthcoming 1.5 years we will work to complete studies in each of the aims. We will establish the *dose-dependence* of hsc recruitment, hematotoxicity, genotoxin exposure dose, and frequency of genetically aberrant cells. Although dose-response relationships were not part of the original experimental design, our unexpected findings that genotoxin exposure of hsc cycling in response to induced hematopoietic stress result may result in persistence of fewer genetically damaged blood cells warrants further investigation. The dose-dependence of our observations has major implications for risk assessment and health effects. These studies should be completed and submitted for publication by the end of 1998. We will also complete our studies to establish whether in vivo exposures to benzene, TCE and radiation induce genomic instability in hsc. These studies should be completed and submitted for publication by March of 1999. Finally, we will continue to characterize the genomic and cellular changes in mice exposed to mixtures of benzene, TCE and radiation as they develop leukemia during the next year.

A Novel Biomarker for Beryllium Sensitization in Humans

Richard J. Albertini, University of Vermont

Research Objective

Beryllium reactive T-lymphocytes can be used as an indicator of sensitization. Traditionally, their presence is detected by an *in vitro* proliferation assay. However, this test is capricious (results varying from day to day in the same laboratory) and insensitive (rarely positive before clinical symptoms). The objective of this project is to obtain and characterize beryllium reactive T-cells from peripheral blood using the *hprt* T-cell mutation assay. T-cells are selected on the basis of their mutation of the *hprt* gene which renders them insensitive to 6-thioguanine in culture. Such mutant populations are expected to be enriched for cells which are proliferating *in vivo* as a result of the sensitizing process. This hypothesis has been verified in a number of studies.

The seven specific aims of this study will: (i) identify the *in vivo* proliferating T-cell clones in sensitized individuals by selecting for *hprt* mutants, (ii) determine T-cell receptor (TCR) gene usages and commonalities among these clones, (iii) demonstrate reactivity to beryllium of these clones, (iv) generate beryllium sensitized T-cells *in vitro* from peripheral blood of the same individual, (v) determine TCR gene usages and commonalities for these *in vitro* derived cells, (vi) compare TCR gene patterns between the *in vivo* and *in vitro* derived clones, and (vii) develop a quantitative PCR (qPCR) method for amplifying the common (and therefore relevant) TCR genes directly from peripheral blood. The last of these is the novel biomarker of early beryllium sensitization.

This report summarizes studies of the first 20 months of this project.

Research Progress and Implications

T-cell Cloning Assays for *hprt* Mutants

Twenty-four (24) peripheral blood samples from 17 individuals reported to be sensitized to beryllium have been obtained. Sixteen cloning assays on samples from ten individuals have found *hprt* mutant frequencies (Mfs) that range from 0.1-87.0 x 10^{-6}. All save three of these (two in one individual) are within the normal range. Therefore, unlike some autoimmune/hypersensitivity diseases, these results provide little support for the expectation that the sensitized individuals will have elevated MF values because of T-cell proliferation. (The remaining peripheral blood mononuclear samples have been cryopreserved for future study.)

TCR Gene Analyses

Sixty-nine wild type and 303 *hprt* mutant isolates, respectively, have been obtained from cloning assays. No evidence of common gene usage was found by sequence analysis of TCR gene variable (BV), junctional (BJ) or hypervariable (CDR3) regions, except for clonal amplifications. Although small clonal amplifications (based on identical TCR gene sequences in two or more isolates) were found among the mutants in many individuals, only one relatively large clone was found, and that in two separate blood samples from one individual.

Studies of Beryllium Reactivity

Because of limited cell numbers, it was necessary to establish autologous lymphoblastoid cell lines as antigen presenting cells. Seven such lines from seven individuals have been established. Others will be as peripheral blood mononuclear cell samples are thawed.

Three beryllium stimulation assays have been performed using random mutant isolates, none of which represented an *in vivo* clonal amplification. All were negative as manifest by lack of sustained antigen driven cell growth *in vitro*. Further challenge assays are being deferred until the hundreds of isolates available for study are prioritized.

Development of a TCR Gene Assay

Studies of TCR gene usage in immunologically reactive cells define only a portion of the genetically encoded antigen binding potential of these cells. Because no commonality of TCR gene usages have been apparent in studies to date, TCR gene usage of the isolates will be determined. Therefore, the TCR gene assay was adapted to our laboratory for this use. As this assay requires multiplex RT-PCR and sequencing of the multiple TCR gene segments (there are 33 TCR gene variable region (AB) families), this adaptation required the acquisition/development of many suitable primers for multiplex PCR analysis. This consumed considerable time.

Generation of Beryllium Reactive T-cell Clones *in vitro*

Attempts to develop T-cell lines directly from peripheral blood have not succeeded using samples from three putatively beryllium sensitized individuals. However, on review of the Beryllium Lymphocyte Proliferation Test (BLPT) results on the 24 blood samples received thus far from the Oak Ridge Laboratory, it was found that all were negative for the samples received. These individuals, however, did have positive test results in the past. We have recently established an alternative source of clinical material.

Summary and Implications of Results to Date

We have determined that putatively beryllium sensitized individuals do not have elevated *hprt* T-cell mutant frequencies. Also, there are no large clonal “mutant runs” among the mutant isolates from these individuals. This may indicate that, in the individuals from whom samples were received, there were no ongoing T-cell proliferations at the time the samples were obtained. (Note that the BLPT status of all the samples received to date suggest that some or all of these samples may not be from individuals sensitized to the degree expected.) Alternatively, this may indicate that sensitized T-cells amplifying in body compartments (e.g. lungs) do not leak to the peripheral blood in this disorder. Another possibility (which may be more likely) is that multiple TCR gene products interact with beryllium antigen complexes and that the reactive cells present among the *hprt* mutants will not identifiable by common TCR gene usage.

Planned Activities

Studies in the coming months will be directed to sorting through these alternatives.

1. Analysis of the TCR gene usage for the mutant and wild type isolates currently available will be accomplished. Common usage pattern here will identify clones as likely candidates that represent beryllium sensitized clones.

2. TCR gene (and) usage patterns will be determined in mass cultures of peripheral blood T-cells obtained from beryllium sensitized individuals and stimulated with PHA or beryllium. This will identify differential TCR usage patterns between the specific (beryllium) vs. polyclonal activator (PHA) stimulated cultures. This differential will identify the patterns that identify *in vivo* derived *hprt* mutants as likely candidates for antigen challenge studies.
3. Continuation of the antigen challenge studies as prioritized by steps 1 and 2.

Additional studies will employ beryllium rather than PHA in some *hprt* T-cell cloning assays. Finally, another source of beryllium sensitized individuals has been developed. All studies will be repeated using samples from individuals who have high BLPT test results on the samples under study. Beryllium sensitized T-cell lines will be directly obtained from peripheral blood from these individuals.

Other Access To Information

There are no formal publications of this work to date. These results are available through the progress reports at the Department of Energy.

Engineered Antibodies for Monitoring of Polynuclear Aromatic Hydrocarbons

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Victoria A. Roberts, The Scripps Research Institute
Qing Xiao Li, University of Hawaii

Research Objective

The long-term goal of this project is to develop antibodies and antibody-based methods for detection and recovery of polynuclear aromatic hydrocarbons (PAHs) and PAH adducts that are potential biomarkers in environmental and biological samples. The inherent cross-reactivity will be exploited by pattern recognition methods. Dr. Karu's laboratory uses new haptens representing key PAHs to derive recombinant Fab (rFab) and single-chain Fv (scFv) antibodies from hybridoma lines and combinatorial phage display libraries. Computational models of the haptens and combining sites made by Dr. Roberts's group are used to guide antibody engineering by mutagenesis. Dr. Li's laboratory develops enzyme immunoassays (EIAs), sensors, and immunoaffinity methods that make use of the novel haptens and antibodies for practical analytical applications in support of DOE's mission.

Research Progress and Implications

This report summarizes work completed in one and one-half years of a 3-year project, with close collaboration between our three research groups. Dr. Alexander Karu's laboratory: We proceeded with the two strategies described in our original proposal. Site-directed mutagenesis was used to correct differences in the rFab N-terminal amino acids that were introduced by the degenerate PCR primers used for gene amplification. The binding constants of the rFabs with the corrected sequences will be compared with those of the parent MAbs, and should be very similar. The 4D5 and 10C10 heavy and light chain sequences are being moved to the pCOMB3H phagemid vector to facilitate selection of new engineered mutants.

We attempted to recover rFabs that bound the benzo[a]pyrene-6- and fluoranthene-3- haptens from the semi-synthetic Fab 2LOX phage display library (Medical Research Council, Cambridge, England). However, PCR analyses showed that only about 10% of the sequences in the original library were intact rFabs. The library had to be depleted of phage that bound to plastic or biotin, as well as phage that lacked a Fab L chain. The remaining display phage that bound the PAH haptens were enriched by about 10^6-fold, but all proved to be nonspecific-binding sequences. Consequently, work with this library was discontinued, and essentially the same protocol was applied to screen the Nissim single-chain Fv (scFv) library, which contained about 10^8 sequences. Six naphthalene-binding scFvs and six phenanthrene-binding scFvs were recovered. We are presently characterizing the PAH cross-reactivity and competitive binding by these antibodies, and panning the Nissim library with the other PAH haptens.

Dr. Qing Li's laboratory: The sensitivity and cross-reactivity of the 4D5 and 10C10 MAbs and rFabs from Dr. Karu's laboratory were measured in EIAs with the various PAH haptens developed earlier. Direct competition EIAs were performed with hapten-horseradish peroxidase conjugates of pyrene and benzo[a]pyrene (BP). Indirect EIAs using different coating antigens were most sensitive: pyrene-1-BSA for the MAbs, BP-6-BSA for rFab 10C10, and phenanthrene-10-BSA for rFab 4D5. EIAs with the rFabs were much more sensitive for 4- and 5-ring PAHs (I50 = 170-230 ppb) than for 2- and 3-ring PAHs (I50 > 3700 ppb). The results showed that selectivity as well as sensitivity of these antibodies to PAHs can be altered over a substantial range by changing the assay format and competing hapten.

Significant progress was also made toward reliable PAH immunoanalysis of environmental and biological samples. Indirect competition EIA was used to compare recovery of BP spikes from 0.5-151 ppb (2-600 nM) in phosphate buffer, tap water, unfiltered Ala Wai canal water, and urine. Recoveries averaged 88 ± 6% to 95 ±13% in buffer and water, and 111 ± 17% in urine. No significant matrix effects were observed with these samples, other than the slightly higher bias in the urine. The EIA results with these samples correlated closely (slope =0.97; r2= 0.99) with values obtained by gas chromatography (GC).

We developed a versatile chelating agent-assisted supercritical fluid extraction method that allowed quantitative (87-106%) recovery of the nonpolar PAHs as well as polar chlorophenoxy pesticides aged in clay soils. This method is being applied to determine bioavailability of PAHs in contaminated harbor sediment.

We also began a study of PAH bioaccumulation in marine coral. Methods were developed for Soxhlet extraction of organics from 50-gram samples into hexane. The recovery of PAHs added as pre-extraction spikes was 85-108%, determined by GC/FID and GC/MS. Porites compressa (a non-endangered species) from unpolluted waters contained 19-23 ng of naphthalene and 114-153 ng of phenanthrene per gram. Immunoaffinity columns prepared by coupling MAb 4D5 IgG to CNBr-agarose gave 68-85% recovery of BP standards in phosphate buffer. We are adapting the immunoaffinity procedure for rapid concentration and cleanup of coral extracts for instrumental PAH analysis.

In collaboration with Dr. Garry Rechnitz, we developed a capacitive immunosensor using MAb 10C10 for detection of PAH-protein adducts as potential biomarkers. The MAb was immobilized on a gold electrode through a self-assembled monolayer of cystamine. Binding of 0.01-6.0 μM BP-BSA and pyrene-BSA conjugates was detected by linear sweep voltammetry as a decrease in the charging current. This and other sensor formats are being tested for measurement of PAHs in solution.

Dr. Victoria Roberts' laboratory: We constructed and analyzed three-dimensional models of the PAH-binding rFabs 4D5 and 10C10, calculated PAH and PAH-linker molecular properties, and performed intermolecular docking studies to understand PAH-antibody interactions. From these results we identified targets for site-directed and combinatorial mutagenesis of the antibodies.

Dr. Li's laboratory demonstrated that the 4D5 and 10C10 antibodies were able to bind BP haptens with either a succinic acid linker at carbon 1 (BP-1) or an isocyanate linker at carbon 6 (BP-6). To better understand these interactions, the shape and electrostatic properties of both haptens were calculated by quantum mechanical methods, and docking to the energy-minimized antibody was simulated using the program AUTODOCK. Linker attachment at C1 caused little perturbation of the electrostatic potential of the BP ring system, unlike the linker on BP-6. Thus, the succinic acid

linker used in BP-1 hapten should be better than the isocyanate linker of BP-6 for selecting antibodies that are optimized to bind BP.

Fifty to 100 docking experiments were done for each molecule. Closely docked positions were clustered together. The most energetically favored cluster found for BP-6 hapten closely matched (within 1 Å) the docked position of the BP-6-isocyanate hapten that evoked the antibody. BP-1 had only one favorable docked position. BP itself docked to rFab 4D5 in four possible binding modes with roughly equal energy, of which two were similar to BP-6, and two were similar to BP-1. Therefore, the 4D5 binding site structure is consistent with hapten BP-1 binding almost as strongly as BP-6. The multiple binding modes found for BP are consistent with the binding constants for different PAHs determined by Dr. Karu's group, and the EIA results obtained by Dr. Li's group with different PAH haptens. The docking results suggested that the binding pocket's shape may be further optimized for better selectivity among the PAHs. The hydrophobic side chains at the bottom of the pocket appeared to be particularly critical for selectivity. Combinatorial mutagenesis of the two segments of the variable heavy chain containing these side chains should produce variants with different PAH binding profiles. The docking studies also revealed possible binding sites for BP that are near, but not in, the binding pocket, providing an explanation for the relatively strong binding of PAH hapten conjugates and PAH metabolite-protein adducts. One molecule of a conjugated protein may present more than one hapten or adduct residue to a single antibody molecule, resulting in binding external to, as well as within the specific primary binding site. These loci may also account for the large percentage of weak non-specific hydrophobic binders that Dr. Karu's group recovered when they used PAH-hapten conjugates to pan combinatorial phage display Fab and scFv libraries.

Planned Activities

During the next six months, the new naphthalene and phenanthrene-binding scFvs will be purified and provided to Dr. Li's laboratory, where they will be rigorously characterized and used in multi-analyte EIAs, sensors, and immunoaffinity methods applicable to real-world samples. The scFv DNA sequences will be used by Dr. Roberts to develop and interpret models of these new PAH binding sites. Dr. Karu's group will continue to derive additional scFvs to other PAH haptens from the combinatorial library, and to select new variants by combinatorial mutation of the 4D5 and 10C10 Fab antibodies.

Human Genetic Marker for Resistance to Radiations and Chemicals

Howard B. Lieberman, Columbia University

Research Objective

The broad objective of the project is to understand the molecular basis for the response of cells to radiations and chemicals, with the pragmatic goal of being able to identify human subpopulations that are exceptionally sensitive to DNA damaging agents. The project focuses on HRAD9, a human orthologue of the fission yeast Schizosaccharomyces pombe gene rad9. S. pombe rad9::ura4+ mutant cells are highly sensitive to ionizing radiation, UV and many chemicals, such as the DNA synthesis inhibitor hydroxyurea. They also lack the ability to delay cycling transiently in S phase or in G2 following a block in DNA replication or after incurring DNA damage, respectively -i.e., they lack checkpoint controls. The attempt by mutant cells to progress through mitosis in the absence of fully intact DNA accounts at least in part for their sensitivity to DNA damaging agents. Cells bearing

rad9::ura4+ also aberrantly regulate UVDE, an enzyme that participates in a secondary DNA excision repair pathway. The key role played by S. pombe rad9 in promoting resistance to chemicals and radiations suggests that the evolutionarily conserved human cognate also has important functions in mammals. The first set of aims in this proposal centers on characterizing the structure and expression of HRAD9, to assess structure/function relationships and potentially link protein activity to a specific tissue. The next set of aims focuses on determining the role of HRAD9 in radio/chemoresponsiveness and cancer.

Research Progress and Implications

This report summarizes work performed after 2 years of a 3 year project. Progress has been made towards completion of all of the specific aims. In collaboration with Dr. Scott Davey at Queen's University (Ontario, Canada), human genomic DNA clones bearing homology to HRAD9 have been isolated and the DNA sequence of the genomic version of the gene has been partially determined. Twelve kbp of relevant sequence has been obtained. This genomic DNA contains 3/4 of the previously determined cDNA sequence and about half the coding region. Six introns and six exons have been identified to date. To aid in the identification of evolutionarily conserved regions of HRAD9, and therefore domains of the human protein likely to be important for function, the mouse version of the gene has been isolated. Mrad9 encodes a 389 amino acid long, 42,032 Dalton protein that is 27% identical and 56% similar to S. pombe Rad9p, and 82% identical and 88% similar to HRAD9 at the amino acid level. Expression of the Mrad9 cDNA in S. pombe rad9::ura4+ cells restores nearly wild-type levels of hydroxyurea resistance and early S phase checkpoint control to mutant fission yeast cells. However, UV resistance is only minimally restored and mutant cells remain sensitive to gamma radiation. Mrad9 genomic DNA was isolated from a mouse 129/SvEv library. The Mrad9 gene was localized to a 15kbp genomic DNA fragment, and contains 10 exons separated by 9 introns. These studies demonstrate the existence of a murine orthologue of S. pombe rad9+, and underscore at least the partial evolutionary conservation of rad9+-dependent checkpoint control mechanisms. Comparison of the amino acid sequences from yeast and mammalian Rad9 proteins reveals several short regions found in all versions of the protein, and these sequences are serving as targets for in vitro mutagenesis to define functional domains.

Northern blot analysis has been performed to determine whether there is tissue-specific expression of HRAD9. RNA from 16 different human tissues was probed with HRAD9, and expression was found to be universal. HRAD9 RNA was detected in heart, brain, placenta, lung, liver, skeletal muscle, kidney, pancreas, spleen, thymus, prostate, testis, ovary, small intestine, colon and leukocytes. However, HRAD9 RNA was most abundant in the liver and detected at the lowest levels in the lung.

Several strategies are being pursued to eliminate or reduce HRAD9 protein levels in human cells to define the biological function of the gene. Interestingly, multiple attempts using anti-sense RNA resulted in overexpression of the gene. Northern blot analysis revealed that HRAD9 RNA was markedly abundant in anti-sense producing versus mock treated human cells, suggesting that HRAD9 may be regulated by a novel feedback mechanism. Preliminary studies of S. pombe rad9 indicate that alteration of one region of the protein may produce a dominant-negative mutation. As an alternative strategy to make human HRAD9 mutant cells, this conserved region will be altered in the gene, and subsequently tested for dominant-negative activity in a human genetic background. Previously, we localized HRAD9 to human chromosome 11q13.1-13.2. Alterations in this region were found by other investigators to be associated with cervical carcinoma. Therefore, HRAD9 was considered a candidate for the gene responsible for this type of cancer, based on its map location and on the role of S. pombe rad9 in cell cycle control, which would be consistent with a tumor suppressor gene. Consequently, the status of HRAD9 in control and cervical carcinoma cells and tissues was examined. PCR was used to amplify regions of the HRAD9 gene, or RT-PCR was employed to generate HRAD9 cDNA from samples. Amplified DNA was then examined by SSCP and limited DNA sequence analysis to identify mutations. Using this strategy, the same polymorphism, a T to C transition, was detected in 3 of 8 independent cervical carcinoma cell lines. This change is in the coding region of the gene, but results in the codon change GGT to GGC, which does not alter the encoded amino acid (i.e., glycine). Furthermore, this polymorphism was found in 7 of 7 primary

cervical carcinoma biopsies. Significantly, two nontumorigenic human cell lines and blood samples from 17 unrelated patients having other types of cancers did not demonstrate this nucleotide change. These results indicate that alterations in HRAD9 are most likely not responsible for cervical carcinoma, but the polymorphism has the potential to act as a genetic marker for predisposition to the disease.

Planned Activities

All of the specific aims described in the original application will be pursued essentially as indicated. These goals include determining the entire sequence of the genomic version of HRAD9, looking at the structure and expression of HRAD9 in normal and cancer cells and tissues, examining the biological consequences of reducing or eliminating HRAD9 expression, and establishing whether HRAD9 expression is regulated.

Other Access To Information

Hang, H., S. J. Rauth, K. M. Hopkins, S. K. Davey, and H. B. Lieberman (1998) Molecular cloning and tissue-specific expression of Mrad9, a murine orthologue of the Schizosaccharomyces pombe rad9+ checkpoint control gene. J. Cell. Physiol. (In press).

Structural Biology of the Sequestration & Transport of Heavy Metal Toxins: NMR Structure Determination of Proteins Containing the -Cys-X-Y-Cys-metal Binding Motifs

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Research Objective

The overall goal of our research is to apply the methods of structural biology, which have been previously used primarily in biomedical applications, to bioremediation. We are doing this by using NMR spectroscopy to determine the structures of proteins involved in the bacterial mercury detoxification system. The research is based on the premise that the proteins encoded in the genes of the bacterial detoxification system are an untapped source of reagents and, more fundamentally, chemical strategies that can be used to remove heavy metal toxins from the environment. The initial goals are to determine the structures of the proteins of the bacterial mercury detoxification systems responsible for the sequestration and transport of the Hg(II) ions in to the cell where reduction to Hg(O) occurs. These proteins are meP, which is water soluble and can be investigated with multidimensional solution NMR methods, and merT, the transport protein in the membrane that requires solid-state NMR methods.

Research Progress and Implications

As of June 1998, this report summarizes work after about one and half years of the three-year award. We have made significant accomplishments in three aspects of the NMR studies of the proteins of the bacterial mercury detoxification system.

NMR spectroscopy is well suited for determining the coordination geometry of mercury bound to proteins because 199Hg is a commercially available stable isotope that has spin S=1/2 and a very

large chemical shift range (more than 3000 ppm) that is highly sensitive to the number and type of ligands. This is particularly true for proteins like merP and merT where Hg(II() is the natural metal ligand. The one-dimensional 199Hg NMR spectra of merP and merT in solution were obtained. There is a single resonance is each spectrum, indicating that there is only one unique Hg(II) bound to each protein. This is the expected result for merP, which has only two Cys residues, but is somewhat surprising for merT where two similar, but distinct metal binding sites are anticipated for the presence of four Cys residues. The chemical shift values observed for Hg (II) bound to both merP and meT are well within the range expected of linear bicoordinate aliphatic thiolate model compounds. Thus, the Hg NMR data demonstrate that the bound Hg (II) has two Cys ligands in both merP and merT.

We determined the three-dimensional structure of merP in solution by multidimensional NMR spectroscopy. This required the preparation of an expression system so that large amounts of isotopically labeled protein could be made and purified. MerP is water soluble, but thought to be weakly associated with the membrane surface. More than 1000 restraints were used in the calculations of the structures of this small 71 residue protein. Both the reduced and metal bound forms of the protein were investigated. Nearly all of the polypeptide is well structured in both forms. Residues-10 – 18, which form the metal binding loop, are the least well-defined portions of the structure. These are also the same residues that have their chemical shifts most strongly perturbed by metal binding; this may have functional significance for the proteins. The dynamics of both forms of the proteins were thoroughly investigated with relaxation measurements at multiple magnetic field strengths. Interestingly, there is a difference in the T2 values, but not other relaxation parameters, for residues 11 – 18 in the metal binding loop, between the two forms of the protein. This can be explained by the residues in the metal binding loop undergoing exchange among multiple conformations, also pointing to a functional significance to the spectroscopic properties of these residues.

Both the reduced and mercury bound forms of the protein have essentially the same global fold, which consists of two antiparallel alpha helices overlaying a four strand beta sheet. The BaBBaB fold defines a class of aB proteins with antiparallel beta sheets and segregated alpha and beta sections. Since this class of proteins includes RNA binding domains, DNA binding domains, acylphosphatases, and phosphoglycerate dehydrogenase regulatory domain, there does not appear to be common functional theme among them. Thus, the protein fold may serve as scaffolding for holding the metal binding loop in a favorable position for binding Hg(II) and then passing it on to different metal binding site in merT for transport across the cell membrane.

All significant differences between the reduced and metal bound forms of merP are in the region of the metal binding loop. This region contains the highly conserved residues GMTCAAC, which includes the two Cys residues that contribute the sidechain –SH groups for metal ligation. Binding of the mercury causes a sleight unwinding of the helix as the two Cys residues become closer. Another difference is in the position of the aromatic residue Phe38 that lies below the metal binding loop. In the reduced form, this sidechain is oriented towards the binding loop; in contrast, the aromatic ring moves closer to the surface of the protein in the mercury-bound form. The movement of this aromatic ring may explain the large chemical shifts observed in the presence of minor structural changes between the two forms of the protein.

MerP is a water soluble, globular protein. However, merT is a highly hydrophobic membrane protein and is completely insoluble in water. Thus, its study necessitates the use of model membrane environments. The availability of two different well-characterized model membrane systems, micelles and bilayers, enables both multidimensional solution NMR and solid-state NMR experimental methods to be applied. The NMR studies require the use of uniformly 15N and 13C/15N isotopically labeled samples. We developed a fusion protein expression system for merT that gave the relatively large amounts needed for NMR spectroscopy.

It is possible to prepare samples of merT in SDS micelles that yield two-dimensional HSQC spectra with excellent resolution, especially considering that it is a highly helical protein with limited chemical shift dispersion. The 13C and 15N resonances in double labeled protein samples are relatively broad because the protein lipid complex reorients in solution relatively slowly. As a result the assignment process, which is a necessary prelude to structure determination, has been proceeding slowly. Nonetheless, we are optimistic that the protein will be assigned in the coming months.

It is also possible to reconstitute purified merT into phospholipid bilayers, the definitive membrane environment for a protein with multiple trans-membrane helices. We are developing a general method for determining the structures of membrane proteins by solid-state NMR spectroscopy. It has two sample requirements. The protein has to be immobilized on NMR timescales by its environment, which occurs in lipid bilayers, and is has to be uniaxially oriented with respect to the direction of the applied magnetic field. This can be accomplished with multibilayers oriented between glass plates. We have obtained solid-state NMR spectra of merT oriented between glass plates, as well as magnetically oriented in bicelles, that demonstrate the presence of trans-membrane helices. The initial two-dimensional solid-state NMR spectra of proteins in this family are promising. The next step is to improve the samples and sensitivity so that three-dimensional solid-state NMR experiments can be applied for resolution among all sites and structure determination of the bilayer samples.

Planned Activities

The immediate goal is to optimize the conditions for solid-state NMR structure determination of merT and its variant protein merF, both of which transport Hg(II) across membranes. Then we will apply the multidimensional solid-state NMR experiments needs to obtain complete resolution of backbone sites and to assign them to specific residues in the protein.

Once the structures of both merP and merT are available, we hope to be able to reconstitute them in a model membrane system and be able to study the transfer of metal ions between them.

Improved Risk Estimates for Carbon Tetrachloride

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Research Objective

The overall purpose of these studies is to improve the scientific basis for assessing the cancer risk associated with human exposure to carbon tetrachloride. Specifically, the toxicokinetics of inhaled carbon tetrachloride is being determined in rats, mice and hamsters. Species differences in the metabolsim of carbon tetrachloride by rats, mice and hamsters is being determined in vivo and in vitro using tissues and microsomes from these rodent species and man. Dose-response relationships will be determined in all studies. The information will be used to improve the current physiologically based pharmacokinetic model for carbon tetrachloride. We will also determine whether carbon tetrachloride is a hepatocarcinogen only when exposure results in cell damage, cell killing, and regenerative cell proliferation. In combination, the results of these studies will provide the types of information needed to enable a refined risk estimate for carbon tetrachloride under EPA's new guidelines for cancer risk assessment.

Research Progress and Implications

As of April, 1998 (18 months into a 3-year project)

Species Differences in Responses of Liver Cytochrome P450 Isozymes to Inhaled Carbon Tetrachloride. The effects of repeated CCl4 inhalation on liver cytochrome P450 isozymes CYP2B and CYP2E1 levels and enzyme activity in rats, mice and hamsters have been determined. The effects vary with species and occurred after only 5 days of exposure.

Inhalation of carbon tetrachloride results in both increases and decreases in the levels of CYP2B in liver. The effect depends highly on exposure concentration within a given species. Hamsters appear to be most sensitive, with induction of protein levels occurring after only 1 week of exposure to 5 ppm. In mice, induction occurs after 1 week of exposure to 20, but not 5 ppm. In rats, induction occurs upon inhalation of 20 and 100 ppm. Inhalation of 100 ppm for 5 days drastically reduces the levels of CYP2B in mouse and hamster liver. Inhalation of 5 ppm CCl4 had no effect on CYP2B enzyme activity after 5 days of exposure. However, inhalation of 100 ppm decreased CYP2B enzyme activity in all species.

Inhalation of CCl4 for 12 weeks resulted in a concentration-dependent increase in CYP2B concentration in rats. CYP2B concentration in mice was decreased in animals inhaling 20 ppm and decreased in hamsters inhaling 20 and 100 ppm. CYP2B activity was decreased in a concentration-dependent manner in rats, mice and hamsters inhaling CCl4 for 12 weeks.

The responses of liver cytochrome P450 isozyme CYP2E1 to CCl4 inhalation also varied widely with species and did not parallel those of CYP2B. CYP2E 1 levels were significantly decreased in mice after 5 days of exposure to 20 and 100 ppm, and in hamsters after 5 days of exposure to 100 ppm.

Species Differences in Responses of Liver Cytochrome P450 Isozymes to Ingested Carbon Tetrachloride. The effects of repeated ingestion of 0.5 and 5 ppm carbon tetrachloride in drinking water on liver cytochrome P450 isozozymes are being evaluated. The 1-week studies have been completed. The 4-week study is underway.

Species Differences in Effects of Inhaled Carbon Tetrachloride on Cytolethality, Histopathological Changes and Regenerative Cell Proliferation In Liver. No lesions were observed at 5 ppm, the current TLV for CCl4.

Inhalation of high concentrations of CCl4 induces hepatic damage and regenerative cell proliferation. Hepatic cytotoxicity, necrosis and cell proliferation were greatest in hamsters, intermediate in mice, and least in rats inhaling 100 ppm CCl4.

Proliferation does not occur at concentrations that induce mild lesions.

Species Differences in Effects of Ingested Carbon Tetrachloride on Cytolethality, Histopathological Changes and Regenerative Cell Proliferation In Liver. No liver lesions were present in livers of rats, mice or hamsters drinking water containing 0.5 and 5.0 ppm CCl4 for 7 days.

Whole-Body Metabolism Studies of Inhaled Carbon Tetrachloride. Whole body metabolism studies have been conducted on rats (100, 250 and 1000 ppm) and mice (100 and 1000 ppm). PBPK modeling was performed using the data. Modeling of the rat data replicated results of a previous study, thus validating the model. Preliminary modeling results on the mouse data indicate that metabolism is under-predicted using body-weight-scaled constants from the rat.

Species Differences in the Toxicokinetics of Inhaled Carbon Tetrachloride. Rats and mice have been acutely exposed for 4 hours to 20 ppm 14C-labeled CCl4. Samples are being analyzed.

Results to date suggest that minimal toxic effects occur at the current threshold limit value for carbon tetrachloride (5 ppm) and that a no observed effect level can be determined for liver cell necrosis and proliferaton.

Planned Activities

Future Directions and Expected Progress

Studies on the effects of ingested CCl4 on liver cytochrome P45O isozymes, cytolethality and cell proliferation will be completed.

The in vitro metabolism of CCl4 by human, rat, mouse, and hamster liver microsomes will be compared.

Studies on species differences in the toxicokinetics of inhaled CCl4 will be completed.

Whole body metabolism studies on mice and hamsters will be conducted.

The current PBPK model for CCl4 will be revised based on the data obtained from the toxicokinetic and whole-body metabolism studies.

Determining Significant Endpoints for Ecological Risk Analyses

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Research Objective

Our goal is to establish a protocol for assessing risks to non-human populations exposed to environmental stresses typically found on many DOE sites. We think that we can achieve this by using novel biological dosimeters in controlled, manipulative dose/effects experiments, and by coupling changes in metabolic rates and energy allocation patterns to meaningful population response variables (such as age-specific survivorship, reproductive output, age at maturity and longevity). This research is needed to determine the relevancy of sublethal cellular damage to the performance of individuals and populations exposed to chronic, low-level radiation, and radiation with concomitant exposure to chemicals. We believe that a scientifically defensible endpoint for measuring ecological risks can only be determined once we understand the extent to which molecular damage from contaminant exposure is detrimental at the individual and population levels of biological organization. Our experimental facility will allow us to develop a credible assessment tool for appraising ecological risks, and to evaluate the effects of radionuclide/chemical synergisms on non-human species.

Research Progress and Implications

This report summarizes work completed midway of a 3-year project that began in November 1996. Emphasis to date has centered on three areas: 1) developing a molecular probe to measure stable chromosomal aberrations known as reciprocal translocations, 2) constructing an irradiation facility where the statistical power inherent in replicated mesocosms can be used to address the response of non-human organisms to exposures from low levels of radiation and metal contaminants, and 3) quantifying responses of organisms living in contaminated mesocosms and field sites.

We have had wonderful success in adapting a molecular technique used to measure stable chromosomal aberrations in human atomic-bomb survivors to a biological dosimeter for determining ecological risks. Stable aberrations, known as reciprocal translocations, unlike others, remain detectable for periods long after the initial exposure. The methodology was a spin-off of the human genome project of the DOE. Until recently, however, technique development and application of the approach for ecological risk analyses would have required a monumental effort for each organism studied. It is now possible to achieve the same goal with much less effort in isolating the necessary probes by using chromosome microdissection techniques followed by polymerase chain reaction (PCR) amplification.

We are excited about our development of the first chromosome-specific probe for a non-mammalian species, the yellow-bellied slider turtle (Trachemys scripta). The technique requires microdissection of specific chromosomes followed by polymerase chain reaction amplification and fluorescent in-situ hybridization. The probe, when fluorescently labeled, ‘paints’ that chromosome in any cell of that species treated with the probe. The labeled DNA is then hybridized back to cells sampled from individuals of the same species that have been exposed to contaminants. Reciprocal translocations that have occurred over the life of the exposed organism can then be quantified by

observing the fluorescent marker on translocated chromosomes. Thus, a biological dosimeter that measures cumulative damage in a long-lived vertebrate is now possible. The yellow-bellied slider turtle was chosen as a model organism for this phase of the work because it can accumulate appreciable doses over a lifetime of 30 years, it has a chromosomal constitution amenable to cytogenetic analysis of aberration induction, it has a wide geographical range and is thus found at numerous DOE sites, and it is mobile enough in both terrestrial and aquatic systems to sample a reasonable range of its contaminated environment. Our development of this tool is fundamental to our determining what constitutes a 'significant risk' in ecological risk analyses. We have conducted in vitro experiments using irradiated turtle fibroblasts to document the efficacy of the molecular probe in detecting reciprocal translocations, and we have also developed dose response curves for total aberrations and reciprocal translocations following acute irradiation. Our second area of advancement is in the design and construction of a mesocosm irradiation facility. This facility will allow us to determine: 1) chromosome damage at various radiation exposures and metal contaminant concentrations, 2) relationships between cellular damage and metabolic rate, 3) treatment effects on an individual's energy allocation pattern, growth and survival. The greatest advantage of using mesocosms (outdoor, above-ground tanks in which artificial pond communities are established) is the ability to replicate treatments such that powerful statistical methods can be used. A location on the Savannah River Site was chosen for the array of mesocosms due to its proximity to the PAR Pond Radioecology Laboratory, its isolation from the general public, and the availability of water and electrical power. Land has been cleared of trees, graded, and storm drains installed. Because we anticipate using turtles, fish and amphibians as model organisms, considerable effort was spent designing a mesocosm suitable for a variety of species. Each individual mesocosm will have a sealed ^{137}Cs source suspended above it, thus designs had to consider the need to homogenize the dose distribution within a mesocosm, and to minimize the dose a human would receive working in the field of 50 mesocosms. A subcontractor recently completed construction of the 50 mesocosms. We have installed a prototype irradiator over one of the mesocosms and our initial dose distributions indicate an unexpected heterogeneity that the manufacturer of the sealed ^{137}Cs source is now trying to remedy.

Our first field experiment was designed to test the effects of contaminants on mosquitofish (Gambusia) and snails (Campeloma) reared in a radioactive seepage basin, metal contaminated site (coal ash basins), and a control pond. The design provided animals that were exposed to each type of stress for the entire study (four months), or for pairwise combinations of stress types during different portions of the study. Surprisingly, all animals transplanted to the metal-polluted site died during the first half of the study, whereas survival in the radiation site and reference site was high. Unfortunately, prior to the scheduled end of the second phase of the study, a prolonged drought resulted in drying of the radiation basin and subsequent loss of animals in that site as well. Although the mortality was disappointing, we acquired valuable dosimetry data from the radiation basins and the lessons learned will be applied in future experiments.

Even though our mesocosm facility is not finished, we have designed it such that organisms can be irradiated from the prototype source we are testing. We are now nearing completion of an experiment that examined the effects of low-level radiation exposure, alone and in conjunction with heavy metal contaminants, on larval salamanders. This is our first experiment conducted in the mesocosm facility and we hope to present results at the Society of Environmental Toxicology and Chemistry annual meeting in November.

Planned Activities

Determine if the probe developed for Trachemys scripta works on other species of turtles (July 1998)

Submit a manuscript entitled Turtle Chromosome Specific DNA Libraries for Ecological Risk Assessment of Irradiated Populations to the Journal of Radiation Biology. The paper describes the development of the probe and the acute irradiation dose-response curve. (August 1998)

Conduct an experiment, similar to what was described above for larval salamanders, using freshwater shrimp (September 1998)

Complete mesocosm facility (May 1999)

Compare dose response of turtle lymphocytes (as opposed to fibroblasts) irradiated in vitro vs. in vivo; conduct dose-rate experiments using turtle lymphocytes (June 1999)

Other Access To Information

Dr. Muhlman-Diaz presented a poster publication detailing the development of the chromosomal probe at the Third International Clinical FISH symposium in Steamboat Springs, CO. Brant Ulsh presented a poster detailing the response of turtle fibroblasts to acute irradiation at the National meeting of the Radiation Research Society in Louisville, KY (for which we won a student travel award).

Estimation of Potential Population Level Effects of Contaminants on Wildlife

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Research Objective

The objective of this project is to provide DOE with improved methods to assess risks from contaminants to wildlife populations. The current approach for wildlife risk assessment consists of comparison of contaminant exposure estimates for individual animals to literature-derived toxicity test endpoints. These test endpoints are assumed to estimate thresholds for population-level effects. For several reasons, uncertainties associated with this approach are considerable. First, because toxicity data are not available for most potential wildlife endpoint species, extrapolation of toxicity data from test species to the species of interest is required. There is no consensus on the most appropriate extrapolation method. Second, toxicity data are represented as statistical measures (e.g., NOAELs or LOAELs) that provide no information on the nature or magnitude of effects. The level of effect is an artifact of the replication and dosing regime employed, and does not indicate how effects might increase with increasing exposure. Consequently, slight exceedance of a LOAEL is not distinguished from greatly exceeding it. Third, the relationship of toxic effects on individuals to effects on populations is poorly estimated by existing methods. It is assumed that if the exposure of individuals exceeds levels associated with impaired reproduction, then population level effects are likely. Uncertainty associated with this assumption is large because depending on the reproductive strategy of a given species, comparable levels of reproductive impairment may result in dramatically different population-level responses. We are working on several tasks to address these problems: 1) investigation of the validity of the current allometric scaling approach for interspecies extrapolation and development of new scaling models; 2) development of dose-response models for toxicity data presented in the literature; and 3) development of matrix-based population models that, coupled with dose-response models, will allow for realistic estimation of population-level effects for individual responses.

Uncertainties associated with the current approach to wildlife risk assessment may have direct impacts on DOE EM satisfactorily fulfilling it's mission in two ways. First, risk estimates may be too conservative and therefore remediation may be recommended when it is not needed. Limited

remediation funds may be spent for insignificant or non-existent risks and possibly cause a net increase in environmental damage due to unnecessary habitat destruction. Second, risk estimates may not be adequately protective and therefore remedial actions may not recommended when they are needed. The consequences of this uncertainty is environmental damage and potential NRDA liability. Either of these alternatives results in inefficient use of limited EM funds. This project will provide the tools to better estimate population-level effects and therefore reduce uncertainty associated with wildlife risk assessments.

Research Progress and Implications

This project is being performed in four, interrelated tasks. Progress on each task is outlined below.

1. Development of a database of avian and mammalian toxicity data. Literature search and data acquisition is ongoing for both acute and chronic data for birds and mammals. We are focusing on 12 contaminants that are being addressed as part of the EPA Ecological Soil Screening Levels for Superfund Sites project. We have obtained access to an extensive wildlife toxicity database from the Denver Wildlife Research Center. This database has provided acute toxicity data for multiple wildlife species for approximately 200 chemicals. In addition, we are extracting data from the National Institute of Occupational Safety and Health (NIOSH) Registry of Toxic Effects of Chemical Substances (RTECS) database. We have obtained data for approximately 150 chemicals and are using these data to identify and acquire primary sources.

2a. Development of Dose-Response models. We conducted a literature search to define modeling approaches currently being applied for human health risk assessment. Based on the results of this search, we adopted a modeling approach that is comparable to that employed by the USEPA for human health risk assessment. A two to four parameter logistic model (number of parameters is determined by the attributes of the dose-response data) is fit to literature-derived toxicity data. The resulting model is then used to define the dose level (and 95% confidence limits) that corresponds with selected effect levels. Example models have been developed for approximately 12 chemicals.

2b. Development of improved methods for interspecies toxicity extrapolation. Allometric scaling, one of the available extrapolation methods, is based on the premise that excretion and metabolism of toxic chemicals are a function of an animals metabolic rate, which varies as a function of body weight3/4. Previous research has indicated that acute mammalian toxicity data scales to body weight3/4, while acute avian toxicity data scales to body weight1. However, because these relationships were derived based primarily on data from drugs, or carbamate or organophosphate pesticides, their applicability to metals and chlorinated hydrocarbons commonly found at contaminated sites is uncertain. To address this issue, we obtained avian and mammalian acute toxicity data for over 200 chemicals for which multiple species had been tested. Mean body weight data for all test species were obtained from the published sources. Lethal dose per animal (LD50 x mean body weight) was calculated for each chemical and test species. Linear regression models of log-transformed lethal dose per animal on log-transformed body weight were developed for each chemical. Body weight scaling factors (e.g., regression slopes) were found to vary widely across chemicals for both birds and mammals. In general, preliminary analyses suggest that the body weight3/4 scaling factor may not be appropriate for extrapolation of acute mammalian toxicity data. Whereas the body weight1 scaling factor may be suitable for acute avian toxicity data. However, due to the wide variability of scaling factors among chemicals, use of chemical-specific scaling may be more appropriate than one general scaling factor.

3. Development of population models for wildlife endpoint species of interest. No progress to report at this time

4. Integration of dose-response, interspecies extrapolation, and population models to provide estimates of population responses associated with varying exposures experienced by wildlife species. No progress to report

Planned Activities

1) The US EPA, in cooperation with the Department of Defense, Department of Energy, state agencies, and industry, has initiated an effort to develop ecological contaminant screening levels for soils at Superfund sites. Brad Sample has been invited to be a member of the working group for the development of toxicity reference values as part of this effort. Methods for interspecies extrapolation and dose response modeling developed as part of this project are directly applicable to the joint EPA, DOE, DoD effort.
2) Two abstracts based on an overview of project and interspecies extrapolation have been submitted for the November 1998 SETAC meeting.
3) We have been invited to present our population modeling research at a USGS sponsored symposium on effects of contaminants on wildlife populations in October 1998. A manuscript of the talk will be published in a peer-reviewed proceedings of the symposium.
4) Draft manuscripts on preliminary interspecies scaling analyses and dose-response modeling are expected to be completed by end of FY 1998.

Bioavailability of Organic Solvents in Soils: Input into Biologically Based Dose-Response Models for Human Risk Assessments

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Howard I. Maibach, University of California at San Francisco

Research Objective

The purpose of this study is to determine the bioavailability of organic solvents following dermal exposures to contaminated soil and water. Breath analysis is being used to obtain real-time measurements of volatile organics in expired air following exposure in rats and humans. Rhesus monkeys will be used as surrogates for humans in benzene exposures. The exhaled breath data is being analyzed using physiologically based pharmacokinetic (PBPK) models to determine the dermal bioavailability of organic solvents under realistic exposure conditions.

The end product of this research will be a tested framework for the rapid screening of real and potential exposures while simultaneously developing physiologically based pharmacokinetic (PBPK) models to comprehensively evaluate and compare exposures to organics from either contaminated soil or water.

Research Progress and Implications

This report summarizes work 7 months into a 3-year project. Method development has produced systems for solvent exposure from soil and water which mimic actual exposure, and for which animals and human volunteers can be safely tested. Soil exposure is generally open to the air (working the soil) while water exposure is generally immersion. For 6-8 hour test exposure, a patch has been developed where soil is contained against the skin by a non-occlusive membrane, while simultaneously allowing volatilization of test solvent to the environment (activated charcoal). The water counterpart is an occlusive glass culture dish, sealed to skin with silicone adhesive. Shorter term exposure is done by one hand immersion in a bucket containing circulating water or soil, the volunteer instructed to move fingers through the water or soil. Human volunteers and animals breathe fresh air via a new

breath-inlet system that allows for continuous real-time analysis of undiluted exhaled air. The air supply system is self-contained and separated from the exposure solvent-laden environment. The system uses a Teledyne 3DQ Discovery ion trap mass spectrometer (MS/MS) equipped with an atmospheric sampling glow discharge ionization source (ASGDI). The MS/MS system provides an appraisal of individual chemical components in the breath stream in the single-digit parts-per-billion (ppb) detectable range for each of the compounds proposed for study, while maintaining linearity of response over a wide dynamic range.

1,1,1-Trichlorethane (methyl chloroform, MC) is rapidly absorbed through rat skin following exposure in soil. In humans, the length of time between exposure and appearance of MC in exhaled breath varies between subject and exposure scenario, but there appears to be a 30-60 minute post application delay. Exposure to solvent in the "hand in bucket" system is proving successful for short-term determinations; the patches are proving successful on both animals and human volunteers for longer exposure. Figures show examples of results.

Planned Activities

Following collection and analysis of all the MC exposure data for rats and humans, studies will be implemented to describe the dosimetry for perchlorethylene, trichlorethylene, benzene following dermal exposures. A working PBPK model for MC will be used as the basis for PBPK models that describe the next three chemicals. Breath exhalation profiles will be determined for these volatile chemicals in rats and humans, except for benzene where Rhesus monkeys will be used to replace humans as study subjects.

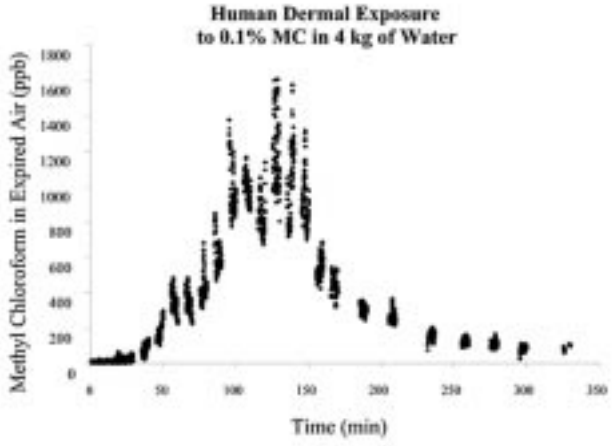

Figure 1

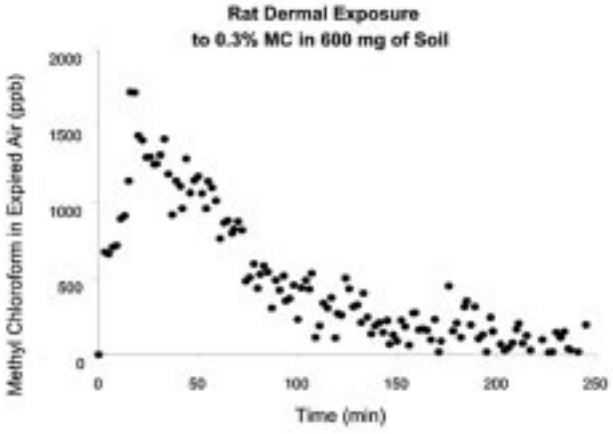

Figure 2

Investigation of Techniques to Improve Continuous Air Monitors Under Conditions of High Dust Loading in Environmental Setting

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John Rodgers, Los Alamos National Laboratory

Research Objective

Improvement in understanding of the deposition of ambient dust particles on ECAM (Environmental Continuous Air Monitor) filters, reduction of the alpha-particle interference of radon progeny and other radioactive aerosols in different particle size ranges on filters, and development of ECAM's with increased sensitivity under dusty outdoor conditions.

Research Progress and Implications

As of May 1, 1998 (1/2 year into the project) the research-prototype 30-cm pulsed ionization chamber (PIC) is assembled and operational with an alpha particle energy resolution of better than 45 keV for 5-MeV alpha particles. Measurements of spectral resolution for alpha particles from radon decay products have been made as a function of filter type and dust loading conditions. So far, a study of ten filter types has found that the best combination of resolution and throughput is obtained with 3.0 μm Millipore fluoropore and 1.0 μm Corning FNMB filters. Experiments with gypsum and Portland cement dust in the size range 1 to 20 um indicate significant degradation in alpha particle resolution for dust loading above about 0.5 mg cm^{-2}. Study of metalized films for possible use as a PIC window indicate a minimum broadening of 5-MeV alpha particle peaks from 43 (no film) to 301 keV (with film) for AVR film type B8 (0.20 mg cm^{-2} polycarbonate). A modified ECAM sampling head, equipped with an optical microscopy system feeding data to a high resolution video data capture and logging instrument, was constructed. This system will enable time-lapse study of dust build-up on ECAM filters and formation of dendrite structures that can reduce alpha-particle resolution.

Planned Activities

Planned activities for the next 6 months:

1) Continue study of the degradation of alpha-particle resolution as a function of filter type and dust loading conditions.
2) Modify and test the large surface area PIC to see if it can be adapted to a design more suitable for use under outdoor conditions.
3) Initiate time lapse microscopic measurements of the build up of dust on ECAM filters with the newly-constructed optical imaging system.

Ultrahigh Sensitivity Heavy Noble Gas Detectors for Long-Term Monitoring and Monitoring Air

John D. Valentine, University of Cincinnati

Kenny Gross, Argonne National Laboratory

Research Objective

The primary objective of this research project is to develop heavy noble gas (krypton, xenon, and radon) detectors for: 1) long-term monitoring of transuranic waste, spent fuel, and other uranium and thorium bearing wastes, and 2) alpha particle air monitors that discriminate between radon emissions and other alpha emitters. A University of Cincinnati/Argonne National Laboratory (UC/ANL) Team has been assembled to complete this detector development project. DOE needs that are addressed by this project include improved long-term monitoring capability and improved air monitoring capability during remedial activities. Successful development and implementation of the proposed detection systems could significantly improve current capabilities with relatively simple and inexpensive equipment.

Research Progress and Implications

As of June 1, 1998, the UC/ANL Team has: 1) made significant progress toward characterizing the fluid transfer process which is the basis for this detector development project and 2) evaluated several radiation detectors and several potential pulse processing schemes. The following discussion describes the progress made during the first year of this project and the implications of this progress.

ANL first developed the fluid transfer process through which heavy noble gases in the atmosphere are preferentially absorbed by certain organic fluids (corn oil has been used most extensively in this project) and can subsequently be degassed by adding a small amount of energy. It is this fluid transfer process that allows the heavy noble gases to be concentrated for enhanced detection. Due to ANL's extensive experience in characterizing this process, this part of the Team is continuing to take the lead in this area. Toward this end a set of experiments was conducted to measure the pressure drop for 3-in-1 oil using structured packing material and comparing with the data for corn oil. The motivation for testing with 3-in-1 oil is that for long-term deployment of our ultrasensitive detectors, untreated corn oil may oxidize with time, lowering the absorption coefficient and degrading the energy utilization (because of increased viscosity caused by oxidation-induced polymerization of oil molecules). For long-term, field-deployed monitoring systems, there may be advantages to using a fluid with an extremely low oxidation potential. One implications that can be drawn from these experiments is that the pressure losses when using structured packing materials are not only small, but are independent of fluid flow rate for both 3-in-1 oil and for corn oil. This important finding will be leveraged in future prototype designs. We also intend to use results from these experiments as input into ANL's ISGA FORTRAN design code for packed column scrubbers to optimize future prototypes.

In addition, UC has assembled and characterized a small prototype fluid transfer system to use as an input to the detector and pulse processing scheme development components of this project. This prototype system is being used in a charcoal-filtered hood to minimize atmospheric emissions and is consequently limited by the size of the hood. Nonetheless, the system behaves as a larger system would, but with much lower efficiencies. Thus, results must be appropriately scaled to realistic system dimensions and efficiencies.

A significant part of scaling prototype results consists of accounting for limited geometry and performance of radiation detectors used in these experiments. Simulations have been developed to model the behavior of detectors and pulse processing schemes used in these laboratory prototype

experiments. Once the simulations are shown to accurately predict lab experiments, they can be used to optimize geometries and performance in these optimized geometries.

To accurately detect and quantify the radioactive heavy noble gas isotopes, a detection scheme which distinguishes between alpha and beta particles, as well as recording gamma-ray spectra, will result in the best system sensitivity. To accomplish this discrimination, potential detector candidates typically consist of one detector for the alpha and beta particles and a separate detector for the gamma rays. A gas proportional detector coupled with a NaI(Tl) scintillation detector is one such promising detector combination. The UC/ANL Team has carefully evaluated a gas proportional detector for use as the alpha/beta detector based on pulse height discrimination. Results indicate that while this proposed scheme has potential for good performance, use with more sophisticated coincidence timing pulse processing schemes which are necessary to accurately quantify isotopic concentrations is not optimal due to poor gas proportional detector timing resolution.

Other potential alpha/beta detectors are being evaluated for use with NaI(Tl) or some other gamma-ray detector. Specifically, plastic and liquid scintillators are being simulated and experimentally investigated. To date, plastic scintillators have been used with NaI(Tl) with superior timing performance as compared with the gas proportional detectors. Pulse shape analysis is being evaluated as a means of discriminating between alpha and beta particles.

One example of the significance of simulating detector performance for guidance is the proposed use of CsI(Tl) flow-cell detectors to accomplish the alpha/beta discrimination. Through radiation transport simulations, it was found that such detectors would need to be prohibitively thin in order to allow gamma-ray emissions to reach the NaI(Tl) detector. Consequently, this type of detection scheme is not currently being pursued further.

Finally, beta/gamma coincidence techniques have been evaluated as a means of enhancing system sensitivity. By only recording decays in which two or more emissions (typically a beta particle or conversion electron and a gamma ray) are detected in coincidence, background counts can be significantly reduced. Such coincidence pulse processing techniques have been evaluated for use with the gas proportional detector/NaI(Tl), plastic scintillator/NaI(Tl), and through simulation the CsI(Tl) flow-cell detector/NaI(Tl) systems. Triple coincidence techniques have also been studied for use with those isotopes that decay by emitting a beta particle followed by a gamma ray and subsequently a conversion electron. Results indicate that background can be virtually eliminated in certain cases.

Planned Activities

In the coming year the UC/ANL Team will continue to characterize and optimize the absorption and degassing of the fluid transfer system in an effort to arrive at a realistic system for field use. One potential complication associated with the fluid transfer is the extent to which air is concentrated by the oil. The simplest way to explore this issue quantitatively is via stable gas mass spectrometry. Experiments are planned for evaluating this complication using air that is spiked with samples of enriched Xe and Kr that will be passed through an oil absorber and de-sorber. Use of isotopically enriched noble gas will enable us to distinguish between our tag gas and entrained natural- abundance Xe and Kr from the air. Mass spectrometric analyses will enable us to accurately quantify the degree of noble gas concentration vs. the degree of air-constituent concentration. The Team will continue to develop simulations of the fluid transfer system, as well as proposed detectors. These simulations will be used to guide further system optimization. In addition, the Team will continue to evaluate detectors and detection schemes for integration with the fluid transfer system. This detector evaluation effort will include the gas proportional/NaI(Tl), plastic scintillator/NaI(Tl), and liquid scintillator/NaI(Tl), as well as any additional detectors that are identified. Along these lines, we will reconsider the use of CdZnTe as a gamma-ray detector to replace NaI(Tl). With the significant recent advances in spectroscopy quality CdZnTe detectors, it may become more favorable to use these detectors coupled with charged particle detectors for air monitoring. With respect to evaluating detection schemes, pulse processing techniques which reduce minimum detectable activities and simultaneously facilitate isotopic analysis will be developed and optimized.

Other Access To Information

The UC/ANL Team recently presented a paper at the 1998 Symposium on Radiation Detection and Measurements describing the small prototype fluid transfer system and its performance. This paper has been accepted for publication in Nuclear Instruments and Methods in Physics Research, Section A and should appear in this journal in late 1998 or early 1999.

High Level Waste

Chemical Speciation of Strontium, Americium, and Curium in High Level Waste: Predictive Modeling of Phase Partitioning During Tank Processing

Andrew R. Felmy, Pacific Northwest National Laboratory

Research Objective

In this research program, Pacific Northwest National Laboratory (PNNL) and Florida State University (FSU) are investigating the speciation of Sr and Am/Cm in the presence of selected organic chelating agents (ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA), and iminodiacetic acid (IDA)) over ranges of hydroxide, carbonate, ionic strength, and competing metal ion concentrations present in high level waste tanks. The fundamental understanding of chemical speciation reactions gained from these studies is also used to propose methodologies for removal of Sr and Am/Cm from organic chelates present in high level tank waste, via competition, displacement or other reactions, without the need for the development of costly and potentially hazardous organic destruction technologies.

Research Progress and Implications

As of May 1998, these studies show that given the expected range in chelate concentrations present in tank waste and the fact that carbonate is present in significant concentration in all tanks, it is likely that the chemical speciation of Sr will be almost certainly unaffected by the presence of IDA and probably also unaffected by the NTA as well. Only HEDTA and EDTA appear to be present at high enough concentration and form strong enough complexes to significantly impact the speciation of Sr in tank waste. In addition, competition with other metal ions present in such solutions, in this case Ca, can effectively displace Sr from the strong chelating agents HEDTA and EDTA, depending upon the concentration of Sr and the competing metal ions. This result indicates that metal ion displacement may represent an acceptable alternative to costly and hazardous organic destruction technologies in reducing the impacts of organic chelates in tank processing, especially given the fact that the chelators represent only a small fraction of the total organic carbon in tank waste. Predictive thermodynamic relationships have been developed for Sr in the presence of mixed hydroxide-carbonate systems and in the presence of competing metals (Ca^{2+}), along with a detailed mechanistic understanding of the important speciation reactions in these system

Considerable progress has also been made in the study of the effects of hydrolysis and carbonate complexation on the displacement of trivalent actinides and actinide analogs from the organic chelates: EDTA, HEDTA, NTA, and IDA. Studies on the solubility of Eu (a trivalent actinide analog) compounds [i.e. $Eu(OH)_3(c)$] have been completed as a function of base concentration in the presence of four organic chelates: EDTA, HEDTA, NTA, and IDA. These studies have shown that high base concentration can displace Eu(III) from all of the organic chelates studied. The effective NaOH concentration for the displacement reaction being dependent on the nature of the specific chelate studied and the chelate concentration. Such data are being used to develop accurate thermodynamic models for trivalent actinide species under high base conditions.

Planned Activities

Plans for FY99 call for completing the temperature dependent thermodynamic model for Sr in the mixed chelate systems, completing the studies that have been initiated on the $EuPO_4(c)$, publishing the results on the $Eu(OH)_3(c)$ in mixed chelate systems, and the studies of solution phase calorimetry. Plans for FY99 also call for extending the CE/MS studies to high ionic strength solutions. Support for studies in outer years will be required to: 1) extend the trivalent actinide model to higher temperatures (>250° C), 2) unravel the speciation of tetravalent actinides (especially Pu(IV)), and

3) verify the modeling predictions and speciation measuremets (CE/MS) in tank waste, specifically complex concentrates from the Hanford site.

Other Access To Information

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f-Element Ion Chelation in Highly Basic Media

Robert T. Paine, University of New Mexico

Research Objective

A large percentage of high-level radioactive waste (HLW) produced in the DOE complex over the last thirty years temporarily resides in storage tanks maintained at highly basic pH. The final permanent waste remediation plan will probably require that liquid and solid fractions be chemically treated in order to partition and concentrate the dominate hazardous emitters from the bulk of the waste. This is no small task. Indeed, there does not exist a well developed molecular chemistry knowledge base to guide the development of suitable separations for actinide and fission products present in the strongly basic media.

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

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

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

Research Progress and Implications

As of 5/1/98 (19 months of 36-month project) the following advances have been realized.

1. Hydrolysis Chemistry

   The pH dependence of the hydrolysis of nitrate salts of Sr(II), Y(III), La(III), Nd(III), and Er(III) have been reexamined by use of pH titrations and nephelometry. Particular attention was given to determining the pH for the onset of hydrolysis as well as the kinetics of particle growth at onset. The pH values for hydrolysis onset generally agree with related data in the literature. Following these measurements we have examined the pH shifts in hydrolysis onset as a function of counterion. We have chosen to study several ions typically present in waste media (e.g., NO_3^-, Cl^-, acetate, oxalate), as well as known chelating anions. A selected collection of these data will be presented in the poster paper. As expected, many of these ions cause significant shifts in the pH for hydrolysis onset due to competing association equilibria. Following these studies we have examined hydrolysis onset shifts caused by new phosphonic acid chelators prepared in our group. Dramatic shifts are encountered in some cases comparable to those observed with EDTA. For example, for La(III) the pH shifts are typically 6 pH units.

   In related work, we have also studied the dissolution properties of lanthanide oxide-hydroxide precipitates by complexing anions. In this regard we have observed that several of our new phosphonic acids are very active at precipitate dissolution. In support of this work, we have recently begun to structurally analyze the precipitates and the dissolution complexes by use of solution and solid-state NMR as well as by X-ray light scattering.

2. New Complexant Development

   Our initial efforts have shown that several phosphonic acids chelate with Ln(III) ions in basic media. In particular, we have found that 1 and 2 are particularly effective. This has led to an ambitious effort to prepare a second group of chelators listed as 3-5, which we expect to have improved extraction characteristics.

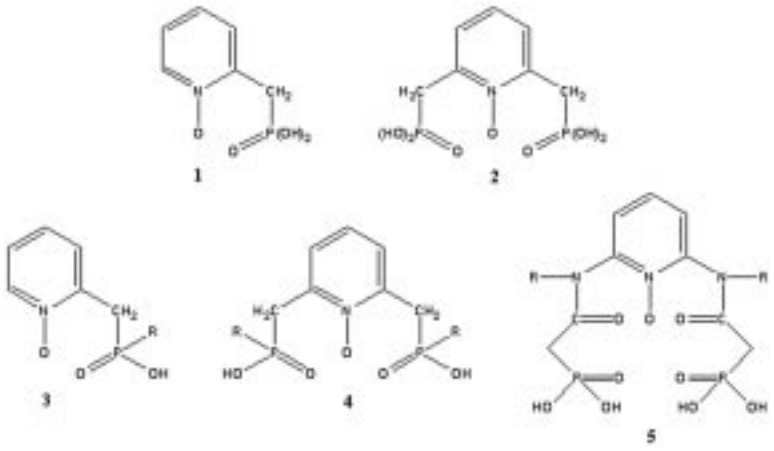

Figure 1

Planned Activities

During the remaining 15 months of the project we expect to continue our study of the interactions of phosphonic acid based ligands with soluble molecular, and oligomeric sol and gel species formed by Ln(III) ions in basic aqueous solutions. We will further characterize the features that are responsible for solubilizing the Ln oxide-hydroxide species and we will employ spectroscopic techniques to determine the nature of the structures formed in soluble complexes. The results will be crucially important to the characterization of soluble species present in tank waste and they will aid in the design of complexants that should be useful for partitioning these and related actinide species in basic media.

Other Access To Information

Two publications are in preparation describing initial results and specific data are available from the PI at UNM.

Synthesis and Characterization of Templated Ion Exchange Resins for the Selective Complexation of Actinide Ions

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O. Manuel Uy, Johns Hopkins University Applied Physics Laboratory

Research Objective

The purpose of this research is to develop polymeric extractants for the selective complexation of uranyl ions (and subsequently other actinyl and actinide ions) from aqueous solutions (lakes, streams, waste tanks and body fluids). Selectivity for a specific actinide ion is obtained by providing polymers with cavities lined with complexing ligands so arranged as to match the charge, coordination number, coordination geometry, and size of the actinide metal ion. These cavity-containing polymers will be produced using a specific actinide ion (or surrogate) as a template around which monomeric complexing ligands will be polymerized. The polymers will provide useful sequestering agents for removing actinide ions from wastes and will form the basis for a variety of analytical techniques for actinide determinations.

Research Progress and Implications

This report summarizes the first nine months of a three year project. During this period polymers have been synthesized using each of the three coordinating ligand monomers: vinyl benzoic acid, vinyl salcylaldehyde and vinyl salcylaldoxime. Uranyl compounds for each of these ligands were synthesized in the mole ratio of one uranyl to two moles ligand and the stoichiometry verified by elemental analysis. Copolymers were synthesized in sets of analogous composition to ascertain optimal uranyl binding ability. For example, nickel vinylbenzoate salt, uranyl vinylbenzoate salt and a vinylbenzoic acid blank were reacted with varying amounts of divinyl benzene (DVB), azobisisobutyronitrile (AIBN), pyridine (solvent), and styrene. The salt and blank concentrations remained constant at 5 weight percent while DVB concentrations varied by 2-4 percent of total reactant weight with AIBN remaining constantly at 1 weight percent. Polymerization was performed in scintillation vials by two different methods. Half of the reactions were performed at 60^{o}C for 024 hours under an N_2 atmosphere in a mineral oil bath, while the remaining half were performed under similar conditions except an ultrasonic bath was substituted for the mineral bath. The resulting polymers ranged from bubbly yellow-brown (uranyl salts) solids to bubbly dark green (nickel salts) solids.

The copolymers made with vinyl benzoic acid and vinyl salcylaldoxime have been examined using uranyl ion luminescence spectroscopy and compared to the luminescence spectra of the isolated analogous compounds. For example, the compounds of uranyl benzoate (UO_2 benzoate2), uranyl vinylbenzoate and the uranyl vinylbenzoate copolymer were investigated by low temperature (77 K) luminescence spectroscopy. The appearance of the spectra show that the structural integrity of the complex is not compromised by the copolymerization process.

The resins were ground into a powder with a cryogenic ball mill and a fraction of uniform size was obtained using sieves. The ground resins were swollen, washed with acetone to remove unreacted monomer and eluted with acid to remove accessible metal ions. After drying, weighed quantities of resin were tested for their exchange capacity by batch loading and extraction. Uranyl ion and competing metal ions were measured using Inductively Coupled Plasma Atomic Emission spectroscopy (ICP-AES) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Preliminary data suggested that for 5 weight percent benzoate complex, 4 weight percent crosslinking and sonication produced the highest capacity polymer. Sonication seems to have a greater positive effect on the polymers made with vinyl salcylaldoxime than those using vinyl benzoic acid. A quantity of the above polymer composition has been applied to sequestration and preconcentration of uranyl from a complex matrix (seawater). The experiment was performed to see if the resin was capable of removing and preconcentrating small amounts of uranium in a mixture of a wide variety of other metals ions prior to their determination by UV-VIS spectrophotometry. The combination of resin extraction and UV-VIS spectrometry yields a simple and inexpensive yet sensitive method for the analysis of uranium in complex matrices. The accuracy and precision of the method were verified by the analysis of a NIST standard sample, NIST 610 trace elements in glass. The photometric analysis employed dibenzoyl methane and gave a linear dynamic range from 500 parts per trillion (ppt) to 1 part per million (ppm) with a limit of detection of 160 ppt. The results of this study will be submitted as an invited paper for a special edition of the Journal Analytica Chimica Acta.

After analyzing the sorbant properties, the polymers were used to fabricate ion selective electrodes. Ground polymer of an appropriate size, 60 mesh, was cast in a polyvinylchloride (PVC) membrane. The membrane was adhesively bonded to a PVC support tube and assembled into a standard polymer membrane electrode. The selectivity and stability of the templated polymer give this electrode advantages over traditional ion selective electrodes. An extensively used electrode does not display a loss of function resulting from solubility of the active ingredient. The templated polymer has greater selectivity for the target ion than does either the monomeric ionophore or the untemplated polymer. The selectivity of the uranyl ion electrode is very high with selectivity coefficients log KU,M around 5 for the interferents tested. A variety of membrane and solution compositions were examined to obtain optimal performance.

Planned Activities

The characterization and optimization of the uranyl polymers will continue. This Summer we are planning a first visit to the Transuranium Laboratory of the Oak Ridge National Laboratory in order to test the polymers with actinide ions other than uranyl. This is expected to occur annually for all three years of the project as more sophisticated resins are developed. The ion selective electrode data will be collected for publication in about six months. The data from the tests with other actinide ions will be used in the next two years to develop both a actinyl complexing resin and resins for individual actinyl and other actinide ions.

Other Access To Information

http://www.rsc.org/is/journals/current/analcoms/anpc9708.htm.

Mechanics of Bubbles in Sludges and Slurries

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Professor Susan J. Muller, Lawrence Berkeley National Laboratory
Guillermo Terrones, Pacific Northwest National Laboratory
William R. Rossen, University of Texas at Austin

Research Objective

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

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

Research Progress and Implications

This three-year research program, which began in FY 1998, is divided into four related problems. Progress has been made in each of the areas of modeling bubble behavior in continuum materials (sludges) from both a solid mechanics viewpoint and separately from a fluid mechanics viewpoint, modeling studies of compressible bubbles in particulate materials (slurries), and experimental studies of bubbles in both sludges and slurries.

The modeling of the bubble/waste interactions from a solid mechanics approach was initiated with a theoretical study to understand the effects that smooth external pressure fluctuations have on the deformation history of a single bubble imbedded in a compressible elastic-perfectly plastic isotropic medium of infinite extent. The problem was approached by solving an outer elastic and an inner plastic problem for each compression and decompression sweep of the pressure cycle, then matching the deformations and stresses at the location of the elastic-plastic boundary. Finite deformations were used to determine the displacements in plastic regions. The general case in which yield and yield in reverse zones alternate with each pressure cycle was considered. A consistent solution of these equations showing the dependence that the bubble volume has during pressure fluctuations has been obtained, and the results show the character of bubble/waste interaction that is intuitively expected.

For continuum modeling from the fluid mechanics viewpoint, the interaction and movement of arrays of bubbles involve a number of scientific issues relating to flows of fluids exhibiting a yield stress. Our interest centers on the region surrounding an expanding bubble where the yield stress is

exceeded and the fluid flows; when the yielded regions for an array of bubbles intersects, the bubbles can move, coalesce, and rise. Because of the computational difficulty associated with solving for the unknown location of the yield surfaces, we are focusing initially on the relatively simple problem of squeezing flow between approaching disks. Existing results indicate that, in a geometry in which the disk radius R is considered infinite, the fluid cannot yield at any point until it has yielded everywhere; in a geometry of finite radius R, however, an unyielded region exists near the center axis. A scaling analysis suggests that the presence of unyielded regions depends on a dimensionless group which is the product of the Bingham number (which approaches infinity) and the square of the gap to radius ratio (which approaches zero). Numerical studies have been initiated to determine where the transition between the infinite domain case (no unyielded regions) and the finite domain case (unyielded regions along the axis) occurs and the effect of length scale on the development of the unyielded regions. The next step is to examine the expansion and contraction of a single bubble in a yield-stress material, then determine the interaction between yielded regions in an array of bubbles. Rheological characterization is being performed concurrently on slurries that simulate the Hanford wastes. These data will ultimately provide parameters for constitutive modeling of the slurries.

For the modeling studies of bubbles in particulate materials (slurries), the pore structure is modeled as a one-dimensional (1-D) network of identical biconical pores with both converging and diverging sections. From this model and the geometric constraints on interface shapes, one can determine the sequence of bubble shapes and volumes as a bubble responds to changes in barometric pressure at constant mass. The analysis defines when jumps in interface position can occur, especially as interfaces penetrate or retreat into pore throats. These jumps mean that not all possible interface positions are observed as the bubble grows. Modeling of interface movement and effective bubble compressibility in a 1-D porespace is nearly complete. Parameters examined include pore shape, bubble size, contact angle, and ambient pressure. Two additional factors must be addressed in the context of this 1-D model: pore heterogeneity and possible bubble breakup at certain jumps.

For the experimental studies, the initial focus is to quantify the effect of small pressure changes on the volume of a single bubble in a waste simulant. The particular challenges for this problem are to measure accurately the induced volume change of non-spherical bubbles while concurrently visualizing the changes in bubble shape. An apparatus for conducting these experiments has been assembled and tested, and it has been designed to automatically conduct repeated pressure cycles. Initial results have been obtained by manually adjusting the pressure controller for a bubble in a transparent simulant of silica particles in an oil with matching refractive indices. Results for bubble volume and shape during pressure cycles have been obtained and clearly show bubble/waste interactions.

Planned Activities

The first year of this project has been devoted to developing the mathematical and computational frameworks and experimental apparatus and methods. While interesting initial results have been obtained, the more challenging problems will be tackled in the next two years. For the solid mechanics modeling studies, the future focus will be on extensions of the current solution to multiple pressure cycles, and the effects of bubble deformation with other yield criteria will be analyzed. In addition, the contribution of neighboring bubbles (multi-bubble problem) to the plastic and elastic deformations will be investigated. For the fluid mechanics studies, a numerical approach is planned with particular emphasis placed on determining the correct form of the boundary conditions; for yield-stress fluids, the location of the yielded region is unusually dependent on boundary conditions set far from the bubble location. For the modeling studies of compressible bubbles in porous media, the results for simple 1-D porous media will be completed, and then the more challenging problem of multiple bubbles in 3-D pore models will be solved. For the experimental studies, we will continue with the single bubble experiments and will also conduct multiple-bubble experiments. These experimental results will then be compared with the modeling results to reconcile the differences between the observed behavior and the different modeling approaches.

Foaming in Radioactive Waste Treatment and Immobilization Processes

Darsh T. Wasan, Illinois Institute of Technology

Research Objective

The objective of this research is to gain a basic understanding of the mechanisms that produce foaming during nuclear waste treatment, to identify the key parameters which aggravate foaming, and to identify effective ways to eliminate or mitigate foaming. The specific goal of this part of the study is to reveal the role of solid particles in colloidal range in foam formation and foam stability. The result of this study will aid in eliminating foaminess in three-phase gas/liquid/solid systems, thereby facilitating implementation of environmental technologies for radioactive waste treatment and waste immobilization processes.

Research Progress and Implications

This report summarizes work completed during the first year of a three-year project. To characterize the foam and identify key parameters for foaminess in a three-phase gas/liquid/solid system, a simulated (non-radioactive) acidified sludge was used. The sludge samples were prepared using PUREX sludge simulant and PHA (Precipitate Hydrolysis Aqueous) was prepared using irradiated precipitate. The pH of the sludge samples was 6.0-6.5 and pH of PHA was 4.0. Both of these samples were prepared at Savannah River Technical Center (SRTC) and were shipped to our laboratory at Illinois Institute of Technology, Chicago. The sludge contained Al (3.8 wt%), Hg (3.5 wt%), Fe (25.5 wt%) on dry basis and noble metals (Rh, Ru, Pd, Ag, Se) in small concentrations. The sludge particles were polydispersed in size varying from about 0.05μm to 10μm. Such a sludge sample is a good model representation of actual nuclear sludge. However, the preparation of sludge in terms of its constituents affects the foaminess.

Experiments were conducted by boiling the sludge in a small-scale evaporator after diluting it with PHA to 10-wt% from its original 20-wt%. The boiling point of the sludge was observed to be 101.5 - 102°C. The parameters which were found to play a key role during foaminess in this kind of three-phase system are the concentration of colloidal solid particles, heating temperature, electrolyte concentration, and composition of organic and inorganic components.

Solid Particles: The first set of experiments were conducted using a supernatant of sludge containing no particles. Foaminess was found to be 15-20%, where foaminess is defined as a percentage of air incorporation by volume. Other experiments with a sludge and PHA mixture showed 200-220% foaminess when solid particles were present. Thus, these experiments revealed that solid particles have a significant effect on foaminess. Besides foaminess, other noteworthy observations are that foaminess in such a system has negligible foam stability, i.e., as soon as the heating was stopped the foam collapsed, and the bubble size is only a few millimeters in diameter. Moreover, during boiling, the solid particle concentration increases and with increasing particle concentration, a maximum in foaminess is observed, which occurred around 18-19 wt% of the solid particle concentration for the sludge studied. The value of foaminess at this concentration was 200-220%. This maximum value of foaminess and solid concentration changes with the method of preparation of the sludge.

This maximum in foaminess can be attributed to the particles' surface properties such as hydrophilicity, hydrophobicity or biphilicity, and polydispersity in particle size. The solid colloidal particles stabilize the foam lamella, which leads to an increase in foaminess. But with an increase in particle concentration, due to an attractive depletion force, particles begin flocculating, and as a result we observe a maximum in foaminess. Therefore, the maximum in foaminess is a direct result

of the balance of two counter effects, namely the particle-particle interactions in the foam lamella leading to foam lamella stabilization before reaching a maximum value in particle concentration, and the attractive depletion force, which is predominant after the maximum concentration, thereby leading to foam destabilization.

Heating Temperature: The rate of generation of a gas is an important factor for foaminess, so the rate at which the gas is evolved has a direct bearing on foaminess. Foaminess increases exponentially with an increase in heating rate. But the noteworthy observation is that the maximum value of foaminess remains unaffected by heating rate.

Electrolyte Concentration: The effect of electrolyte concentration in sludge was studied by using the different diluting media: water, supernatant and PHA. Results showed comparatively lower foaminess in the case where supernatant and PHA are used to dilute the system. This observation can be explained by the fact that the lower foaming system has a higher electrolyte concentration. Besides foaminess, foam texture is also affected by electrolyte concentration, and with a higher concentration the foam lamella size becomes smaller. Further, as the electrolyte concentration increases during the boiling process, the particle-particle attraction improves, resulting in particle flocculation.

Organic and Inorganic Components: During the initial period of sludge boiling, higher foaminess is observed. As soon as the heating is started, the organic components and the decomposition of inorganic components lead to an evolution of a gas which causes an apparent increase in foaminess.

It is concluded that foaminess of the sludge is due to the presence of colloidal particles and has a maximum when particle concentration is increased. The foaminess increases with heating due to the higher gas bubble generation. With an increase in electrolyte concentration, the foam bubble size decreases. The presence of volatile organic components in the sludge leads to higher foaminess.

Planned Activities

The present study clearly revealed that the colloidal particles present in the sludge are the important cause for the foaminess observed. In the next year experiments are planned to study the effect of particle surface properties such as hydrophilicity, hydrophobicity and biphilicity of solid particles. One of the model systems proposed for our future experiments is a suspension of silica particles which are present in the sludge. We plan to use our newly developed capillary force balance technique to understand particle-particle interactions in causing foaminess and foam stability. Based on the results of these experiments, we will examine an antifoaming system which is able to mitigate foaminess at high temperatures.

Dynamic Effects of Tank Waste Aging on Radionuclide-Complexant Interactions

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Research Objective

The overall objective of this project is to provide a scientific basis for safely processing complexant-containing high-level tank wastes for disposal. Our key goals are to identify a means to prepare

realistic complexant-containing tank waste simulants, and to use those simulants to determine the relative importance of organic complexants and their breakdown products on the partitioning of important radionuclides. These goals will be accomplished by artificially aging complexant-containing tank waste simulants using microwave, ultrasound, and photolysis techniques. The simulants will be compared to samples of actual Hanford tank wastes to determine the most realistic aging method, on the basis of the organic fragmentation and the partitioning behavior of the important radionuclides ^{90}Sr, ^{99}Tc, and ^{239}Pu. Also, we will use our simulant aging process to investigate the relative effects of chelator degradation products on the partitioning of important radionuclides from the waste. Using NMR-active labels in the chelators, we will use a combinatorial approach of generating multiple chelator fragments in a single experiment and then determining which fragments have a negative effect on the separations chemistry. Our successful completion of this goal will specifically identify the most problematic organic fragments in complexant-containing waste and provide the basis for developing successful treatment strategies for these wastes.

Research Progress and Implications

This report summarizes work carried out at Los Alamos during the first 8 months of a 3-year project. The report reflects only one month of effort by New Mexico State University collaborators, because of delays in allocating funding to that institution.

Laboratory aging of tank waste simulants: A key problem in developing treatment schemes for nuclear tank wastes is that samples of the wastes are exceedingly difficult to obtain, transport and handle in the laboratory. Although simulated wastes are a safe and inexpensive means for other researchers to become involved in tank waste remediation studies, freshly prepared simulants do not reproduce the partitioning behavior of actual tank waste samples. Therefore, one of our goals is to devise a method for preparing a realistic tank waste simulant that truly behaves like actual tank waste.

To date, we have devoted extensive effort toward the organic analysis of complexants in simulants. We established a procedure for formulating and preparing a simulant of any given tank waste supernatant, by combining analytical data and predictive models based on the history of processing at Hanford. Focusing on Hanford Tank SY-101 supernatant, we have developed a method for esterifying the chelators so that they can be separated from the high ionic strength, alkaline simulant matrix by liquid-liquid extraction. Analysis of the chelators by gas chromatography provides quantitative information on changes in the simulant, but newly formed chelators are difficult to identify without further characterization. We are currently setting up an atomic emission detector that will enable identification of these daughter chelators. Some difficulties remain in the analysis. For example, the important parent chelator HEDTA is not detected by our method. New Mexico State chemists will be working on this problem.

Our aging experiments are difficult to interpret but clearly show rapid changes in the organic composition of the simulants upon heating. We are delaying experiments with actual tank wastes until problems with the analytical method are resolved. Meanwhile we have begun to study the influence of catalytic metals such as rhodium, ruthenium and palladium. These metals are believed to play a significant role in organic reactivity of Savannah River tank wastes, and undoubtedly have an impact on Hanford wastes as well. We are currently testing a hypothesis that catalytic reduction of pertechnetate by hydrogen gas is responsible for formation of intractable technetium species in organic-rich tank wastes.

Effect of individual complexants on radionuclide separation: Over 50 chelator decomposition products have been previously identified in aged tank wastes, most of which are potential chelators themselves. Reconstructing the radionuclide speciation from a simple inventory is impossible because known stability constants for the metal-ligand combinations are limited. We will be using a combinatorial approach of simultaneously generating multiple chelator fragments in a single solution, and evaluating the most significant chelator-radionuclide interactions through a combination of spectroscopic and radiochemical methods.

We have surveyed the impact of several commercially-available complexants on the partitioning behavior of Sr^{2+} and Ce^{4+} (a Pu^{4+} surrogate) from a simplified simulant. To obtain reliable distribution

coefficients, we eliminated the transition metal cations from this simulant to prevent metal hydroxide precipitation. These preliminary experiments showed that radionuclide partitioning onto the chelating resin Diphonix was strongly affected by the parent polycarboxylate chelators EDTA, HEDTA and NTA. However, we have not observed any significant interactions with plausible daughter chelators. Additional chelators will be synthesized at New Mexico State and submitted to Los Alamos for testing.

Planned Activities

Year 1: (a) Analyze organic content and partitioning of Sr, Tc and Pu from actual tank waste samples. (b) Carry out simulant aging experiments and analyze organic content. Repeat selected aging experiments and analyze radiochemical partitioning behavior.

Year 2: (c) Analyze mechanisms and outcomes of organic transformations using GC/MS and NMR methods. (d) Analyze key radionuclide-chelator complexes in aged simulants using heteronuclear shift correlation NMR experiments.

Other Access To Information

Future manuscripts will be posted on the web as they become available (**http://mwanal.lanl.gov/CSTftp/113311/RMChomepage.html**).

Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation

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Research Objective

The broad objective of this project is to provide quantitative mechanistic information relevant to: (i) the extent and nature of radiation-induced chemical modification of the nuclear defense waste that occurs during storage, and (ii) the extent of accumulation of peroxynitrite in the waste and its potential use in remediation. Within this context, the specific goals are:

To determine the radiochemical yields of peroxynitrite in chemical mixtures simulating the various phases (salt cake, slurry, supernatant) of radioactive waste;

Through mechanistic studies of metal- and CO_2-catalyzed oxidations by peroxynitrite, to estimate the extent of peroxynitrite-mediated oxidative degradation of organic waste components and determine the feasibility of using peroxynitrite in remediation technologies, e.g., for the destruction of organic complexants and the removal of chromium for more efficient vitrification.

Research Progress and Implications

This report summarizes work after the first year of a three-year project. The following studies either have been completed or are in progress:

Oxidation of Peroxynitrite by Radiolytically-Generated Inorganic Radicals (publication 1)

The reactivity of the peroxynitrite ion, $ONOO^-$, toward a number of inorganic radicals was determined using pulse radiolysis techniques. Rate constants for oxidation of the $ONOO^-$ ion by the carbonate,

azide, and chlorine dioxide radicals were measured from their decay kinetics to be 7.7×10^6, 7.2×10^8, and 3.2×10^4 $M^{-1}s^{-1}$, respectively. For the hydroxyl radical, the rate constant of 4.8×10^9 $M^{-1}s^{-1}$ was obtained using competition kinetic analysis. For the first time the oxidation potential of the $ONOO^-$ ion was estimated as 0.8 V from kinetic data; the oxidation product decomposes to produce nitric oxide and molecular oxygen. Although thermodynamically favorable, oxidation of $ONOO^-$ by the nitrogen dioxide radical was not observed; an upper limit of 2.5×10^4 $M^{-1}s^{-1}$ could be set for this reaction.

The implications of these results for the waste chemistry are: (i) oxidation of peroxynitrite may be, at least in part, responsible for the generation of nitric oxide emitted by the waste tanks; (ii) nitrogen dioxide, which is the dominant oxidizing radical produced by radiation in the waste, does not scavenge peroxynitrite.

Mechanism of Peroxynitrite Decomposition (publications 2 and 3)

In order to resolve a long standing controversy about hydroxyl radical production via the proton-catalyzed decomposition of peroxynitrite, this reaction was studied in the pH range 5-10. While nitrate was the only product in the acidic solutions, in neutral and alkaline media nitrite and O_2 were also produced, with the oxygen yields reaching 80% of the stoichiometrically attainable at pH 10. Addition of the free radical scavengers (DMSO, alcohols, acetate, etc.) inhibited O_2 formation in a manner that was quantitatively consistent with their reactivity toward the $\cdot OH$ radical. Excess of nitrite reversed this inhibition at pH above 8, but was itself inhibitory under more acidic conditions. No O_2 was produced in the presence of CO_2. An eight-step radical mechanism which requires a generation of the free $\cdot OH$ radical with 30-35% yield was proposed to account for this unique reaction behavior. Upon numerical integration, the proposed mechanism accurately duplicated all experimental data. Because there are no adjustable parameters, the calculations provide a particularly stringent test of the mechanism unambiguously establishing that a free $\cdot OH$ radical is generated during proton-catalyzed peroxynitrite decomposition.

The implications of these results for the waste chemistry are: (i) decomposition of peroxynitrite can be an important source of oxygen within the alkaline waste; (ii) because upon protonation peroxynitrite generates an extremely reactive hydroxyl radical, it is capable of indirectly oxidizing virtually every organic compound found in the waste.

Oxidative Dissolution of Chromium(III) by Peroxynitrite (work in progress)

In strongly alkaline solutions, peroxynitrite rapidly oxidized freshly precipitated chromium(III) hydroxide to a soluble chromate with a stoichiometric ratio [chromate]:[$ONOO^-$] close to 1:3. Aging of the precipitate resulted in deceleration of the reaction and increase in the relative consumption of $ONOO^-$. Immediately upon initiation the reaction kinetics was first-order in both Cr(III) and $ONOO^-$, however the order in $ONOO^-$ decreased during the course of reaction indicating a possible change in mechanism. The initial reacion rates were independent of the hydroxide concentration and ionic strength. A working hypothesis concerning the effect of aging is that a massive hydroxide is gradually formed making the inner Cr atoms unaccessible to the oxidant. A significant effect of additional transition metals on the reaction kinetics was observed. For example, in mixed Cr-Mn hydroxide the reaction was not only faster, but was also relatively insensitive to aging and did not decelerate with time. The reaction went to completion within tens of minutes, whereas for pure chromium hydroxide reaction took hours or days depending on the age of Cr hydroxide. Reaction rates linearly increased with [$ONOO^-$] and [Cr(III)] and showed a complex dependence upon the Cr/Mn ratio. In contrast, addition of Cu(II) in quantities comparable with that of Cr(III) inhibited formation of chromate, an effect that was attributed to a catalytic decomposition of peroxynitrite by copper ions. Importantly, Fe(III) hydroxide, which is abundant in the waste tanks, had no inhibitory effect on the rate of chromate formation.

The implication of these findings for the waste remediation is: it appears that peroxynitrite has a potential for being considered as an oxidant for removing precipitated chromium from waste sludges, which will improve their compatibility with vitrification methods for disposal.

Planned Activities

Second year: Studies of the yields and mechanisms of radiation-induced peroxynitrite generation in solid nitrate and nitrite and their concentrated solutions. Finishing studies of oxidative dissolution of chromium.

Third year: Mechanistic studies of metal- and CO_2-catalyzed oxidation of organic complexants by peroxynitrite. Developing generalized dynamical model for the peroxynitrite reactivity pathways in the radioactive waste.

Other Access To Information

1. Goldstein, S.; Saha; A.; Lymar; S. V., Czapski, G., "Oxidation of Peroxynitrite by Inorganic Radicals: A Pulse Radiolysis Study", J. Am. Chem. Soc., (**1998**), in press.
2. Lymar, S. V.; Hurst, J. K., "Radical Nature of Peroxynitrite Reactivity", Chem. Res. Toxicol. (**1998**), in press.
3. Coddington, J. W.; Hurst, J. K.; Lymar, S. V., "Hydroxyl Radical Formation During Peroxynitrous Acid Decomposition", Proc. Natl. Acad. Sci. USA, submitted.

Chemical Speciation of Inorganic Compounds under Hydrothermal Conditions

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Research Objective

To obtain the chemistry of metallic solute ions under aqueous and hydrothermal conditions in order to obtain key insights pertinent to the removal of toxic wastes. Elements present in Hanford tank wastes will be investigated to get a better understanding of how the high temperatures involved in vitrification will affect the hydrolysis-polymerization reaction.

Research Progress and Implications

In the following summary of our x-ray absorption fine structure (XAFS) measurements under aqueous and hydrothermal conditions, most measurements below the critical temperature (375° C) were taken at about 200 bar pressure, while at supercritical temperatures the pressure was about 600 bar.

Chemistry of Na_2WO_4 Under Aqueous and Hydrothermal Conditions

Tungsten, molybdenum, vanadium and, to a lesser agree, chromium, niobium and tantalum form isopolymetallates, polymeric species of rather complicated structure and complex chemical equilibria, in aqueous solution upon acidification. Except Tantalum, all of these elements are present in the Hanford tank wastes and it is not well understood how the high temperatures involved in vitrification

will affect the hydrolysis-polymerization reaction. In March 1998, we launched a series of XAFS experiments to resolve these questions. Measurements were obtained for 0.2 molal tungstate solutions as a function of temperature (to 200° C) and as a function of starting pH. The outcome of these measurements is providing key insights into this chemistry as follows:

1. A change from tetrahedral to octahedral coordination of the oxygen atoms around the tungsten center atom can be detected upon increasing extent of polymerization.
2. At least one new feature shows up in the Fourier Transform of the k-weighted Chi plot (closely related to a radial distribution function) which is unambiguously attributed to a tungsten-tungsten scattering path, only present in the polymeric species.
3. Perhaps most interestingly, the XAFS data indicate a higher extent of polymerization at higher temperatures for a given starting pH.

In order to confirm this finding and to obtain complementary pieces of information, which would assist a thorough analysis of the XAFS data, high temperature, high pressure IR spectra have been acquired for these tungstate solutions. These measurements have been carried out to even an higher temperature of 400° C and, as preliminary result, do confirm the trends observed with the XAFS experiments. These IR measurements will allow a quantitative analysis of the monomer-polymer equilibria since the IR band of the tetragonal monomer is nicely resolved and does not interfere with the resonances of the bands due to polymer species. Each of the resonant frequencies of all resolved tungstate bands shows a temperature dependence, providing further information on the strengths of the tungsten oxygen bonds. This first detailed structural characterization by XAFS and IR of hydrothermal polymerization of isopolymetallates will allow us to model and predict the colloid chemistry which is of relevance to the early stages of tank waste vitrification.

Future XAFS work will extend the above studies not only to higher temperatures but will also include studies of molybdenum, chromium and vanadium. The studies are planned for our first visit to the Advanced Photon Source of Argonne National Laboratory in August.

Chemistry of $NaReO_4$ Under Aqueous and Hydrothermal Conditions

The results of ambient temperature/pressure and high temperature/pressure (i.e., hydrothermal) X-ray Absorption Spectroscopy (XAS) measurements on the $NaReO_4$-H_2O system have also provided significant new information. We are using Re as a surrogate for the radionuclide ^{99}Tc, which is typically encountered in nuclear waste streams [Darab]. The Re LIII white line energy (as determined by the maximum in the XAS spectra) for $NaReO_4$(s) was determined to be 10,544.5 eV while a 0.2m $NaReO_4$(aq) solution measured at ambient temperature/pressure exhibited a white line energy of 10,542.6 eV-a shift of -1.9 eV in going from a crystalline form to an aqueous solution. Since data points were collected every 0.3 eV, this shift is significant. We do not believe that the Re^{7+} species (i.e., ReO^{4-}) is being reduced through a decrease in the formal oxidation state of Re under these conditions, but rather that there are subtle variations occurring in the electronic charge density due to difference in chemistry. For example, the proximity of the Na^+ cation to the ReO^{4-} oxo-anion in $NaReO_4$(s) may certainly be different than that in solution, producing a difference in the charge distribution around the Re central atom.

As the temperature and pressure were increased, there was a systematic increase in the Re LIII white line energy to 10,544.4 eV-within experimental error equal to that for $NaReO_4$(s) (10,544.5 eV) as well as Re_2O_7(s) (10,544.1 eV). This may indicate a return to a NaReO4(s)-like environment for hydrothermal solutions of $NaReO_4$ at 425° C. Alternatively, both crystalline Re_2O_7 and crystalline perrhenic acid, $HReO_{4.0}.^5H_2O$ or $Re_2O_{7.2}H_2O$, contain binulcear Re species: a tetrahedral Re-O complex sharing a corner with an octahedral Re-O complex, i.e., $O_3Re\text{-}O\text{-}ReO_3(H_2O)^2$ [Cotton]. Thus, the shift in white line energy could also represent an approach to $Re_2O_{7.x}H_2O$-like structures in hydrothermal solutions of $NaReO_4$ at 425° C. Detailed analyses, once performed, on the EXAFS obtained from these experiments will prove useful in elucidating the change in chemistry as the temperature and pressure are increased.

Finally, upon increasing the temperature from 425° C to 500° C, the Re LIII white line energy dropped significantly to a value of 10,543.2 eV-which is very close to that obtained from ReO_3(s)

(10,543.5 eV). Thus, under these conditions, we believe that the Re^{7+}, which is the most probable oxidation state at 425° C, is reduced to Re^{6+} at 500° C. Again, once detailed analyses are performed on the EXAFS obtained from these experiments, additional insight will be gained pertaining to the chemical changes taking place between 425° C and 500° C.

Chemistry of Cu(II) Under Aqueous and Hydrothermal Conditions

Scoping studies of the redox chemistry of Cu(II) were also completed in the spring XAFS runs at the Brookhaven synchrotron. Four different inorganic and organometallic copper compounds were tested at that time. To our surprise most of the redox chemistry was occurring well below 200° C. In addition we discovered that many of the special, high-temperature metal alloys present in the pumping and transfer system and in the XAFS cell itself were very likely reacting with the copper compounds. Thus, for all subsequent runs we will use only Pt-Ir and diamond for all wetted surfaces. The redox chemistry of Cu(II) (and of other ions such as Fe(III) and chromate) remains high on our list for future XAFS studies.

In addition to investigating by XAFS the frequency structure around solutes, we are fabricating instrumentation to measure their structure also with anomalous diffuse elastic x-ray scattering (ADEXS) for x-ray energies near the absorption edge of the solutes. The ADEXS complements the XAFS measurements because they can detect the more spatially smooth contributions to the pair distribution function that XAFS cannot detect. This allows information beyond the first condition shell that usually is invisible to XAFS. However, this information is at the expense of sensitivity to dilute solute concentrations that XAFS can detect. The combination of XAFS and ADEXS gives a more complete picture of the chemistry than can be obtained with either alone. The ADEXS measurements will be performed using the undulator A beamline at the PNC-CAT facilities in the Advanced Photon Source, a third-generation synchrotron radiation x-ray source. The elastic portion of the scattered x-rays will be detected by a Rowland circle spectrometer under construction.

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Planned Activities

X-ray Scattering

In addition to investigating by XAFS the aqueous structure around solutes, we are fabricating instrumentation to measure their structure also with anomalous diffuse elastic x-ray scattering (ADEXS) for x-ray energies near the absorption edge of the solutes. The ADEXS complements the XAFS measurements because it can detect the more spatially smooth contributions to the pair distribution function that XAFS cannot detect. This allows information beyond the first coordination shell that usually is invisible to XAFS. However, this information is at the expense of sensitivity to dilute solute concentrations that XAFS can detect. The combination of XAFS and ADEXS gives a more complete picture of the chemistry than can be obtained with either alone. The ADEXS measurements will be performed using the undulator A beamline at the PNC-CAT facilities in the Advanced Photon Source, a third-generation synchrotron radiation x-ray source. The elastic portion of the scattered x-rays will be detected by a Rowland circle spectrometer under construction. The ADEXS apparatus will be commissioned in the fall of 1998. The first measurements will be started in January 1999. These and subsequent measurements will be compared with the XAFS analysis on similar solutions from spring of 1999 until August 2000 in order to determine the full pair distribution function about the solutes as function of temperature and pressure in the subcritical and supercritical phases.

Radiation Effects on Transport and Bubble Formation in Silicate Glasses

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Research Objective

To study the fundamental chemistry of radiation damage in silicate/borosilicate glasses and simulated high-level nuclear waste (HLW) forms. Special emphasis is on delineating molecular processes crucial for understanding the aggregation of defects and formation of oxygen bubbles. The knowledge obtained will provide the needed scientific basis for extrapolating long-term behavior of stored radiative waste glass forms.

Research Progress and Implications

This report summarizes the first 6 months of a 3-year project. The following issues have been addressed: (i) the production of radiolytic oxygen, (ii) the chemistry of hydrogenous species, and (iii) the effect of glass composition and microstructure on the formation and accumulation of metastable point defects.

1. Radiolytic oxygen. While the earlier studies indicated that during electron bombardment of silicate glasses the yield of interstitial O_2 was ca. (1-5) x 10-6 eV-1, recent transmission electron microscopy (TEM) studies suggested that upon (c)-radiolysis this yield is 102-103 times higher. The latter estimate places the onset of the O_2 bubble formation in the HLW forms from 1012 rad (1-10 kyr of storage) to 108-109 rad (several years of storage). Questions have been raised about the validity of these TEM measurements (The dose accumulated during the TEM inspection could be considerably higher than the initial (c)-radiation dose.) Our effort is concentrated on measuring the yields of radiolytic gases using less invasive techniques:

   Glasses of various compositions were irradiated with 3 MeV electrons to 109-1010 rad. Two approaches have been used to measure the gas evolution, (i) thermally outgassing the glass samples followed by mass spectrometric analysis of the evolved gases, and (ii) detecting the interstitial O_2 in-situ using laser-induced emission of $^1O_2$ in the near IR. While the latter approach is still under development, the outgassing experiments have shown that the yield of radiolytic O_2 is actually lower than the lowest earlier estimates. (Since the 0.1-10 keV electrons used in the earlier studies had short penetration depth, some oxygen was produced due to destruction of the charged surface.) In the dose regime studied, the yield of radiolytic O_2 is comparable to the yield of radiolytically desorbed N_2 and by 10-100 times less than the yield of radiolytically generated/desorbed CO_2.

   Particularly low yields of O_2 were observed in the simulated HLW forms, apparently due to uptake of O_2 by metal cations. The implication of our study is that the concentration of O_2 at which the bubbles are formed will accumulate only after 1-10 kyr of the storage. The bubble formation can be further delayed by partial reduction of metal oxides during the glass manufacturing.

2. Hydrogenous species. Mobile, short-lived hydrogen atoms generated by radiolysis of the OH groups anneal the point defects and ameliorate the radiation damage. We undertook a detailed study of the H and D atoms in boron oxide glasses; this study complements our previous work on the H/D atoms in fused silica. Diffusion coefficients of the H/D atoms and the rates of their collisions with transitional metal cations and other defects were measured, and the mechanism of the H atom generation was determined. In particular, it has been shown

that in the boron oxide glass (in contrast to silica) the H atoms decay in spur reactions with other H atoms and/or metastable point defects. The former reaction yields H2 which coalesces into bubbles at 108-109 rad (compare to 1012-1013 rad for O_2) causing swelling of the glass. Our study resolves several issues concerning the fate of hydrogen in oxide glasses, it also provides a reference system to study radiation-induced volatilization in glasses, in the dose ranges that are readily available to most researchers.

3. Defects in complex glasses. Commercial glasses that exhibit highest leach resistance is microheterogeneous alkali alumo-borosilicate glasses. In such glasses, 1-to-10 nm islets of the boron-rich phase are imbedded in a silica-rich matrix. Since many silicate and borosilicate glasses (including some HLW forms) are phase-separated, the question arises how the radiation damage is distributed between the phases. Using advanced methods of pulsed EPR, we have demonstrated that the radiation damage in borosilicate glasses is concentrated in the boron-rich islets, regardless of their mass fraction. Our work suggests that by using microscopically phase-separated glasses one can achieve the least radiation damage to the bulk of the glass combined with the highest chemical resistance.

Planned Activities

1. We will continue to study the formation and decay of radiolytic O_2, with an emphasis on the role of redox reactions with metal ions and point defects. Our current priority is to improve the accuracy and reliability of the outgassing experiments and to develop optical spectroscopies that would complement these measurements.
2. We have demonstrated the potential of pulsed EPR to sort through many types of paramagnetic defects present in irradiated glasses. These studies will be extended to include alkali silicate, alumosilicate, and borosilicate glasses doped with transition metal cations.

Ionizing Radiation Induced Catalysis on Metal Oxide Particles

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Research Objective

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

This project focuses on using ionizing radiation (α,β,γ) to catalytically destroy organics over oxide materials through reduction/oxidation (redox) chemistry resulting from electron-hole (e^-/h^+) pair generation. Conceptually this process is an extension of visible and near-UV photocatalytic processes known to occur at the interfaces of narrow bandgap semiconductors in both solution and gas phases. In these processes, an electron is excited across the energy gap between the filled and empty states in the semiconductor. The excited electron does reductive chemistry and the hole (where the electron was excited from) does oxidative chemistry. The energy separation between the hole and the excited electron reflects the redox capability of the e^-/h^+ pair, and is dictated by the energy of the absorbed photon and the bandgap of the material. The use of ionizing radiation overcomes optical transparency limitations associated with visible and near-UV illumination (γ-rays penetrate much farther into a solution than UV/Vis light), and permits the use of wider bandgap materials (such as ZrO_2) which possess potentially greater redox capabilities than those with narrow bandgap materials.

Experiments have been aimed at understanding the mechanism(s) of γ-radiocatalysis and extending the body of knowledge about e^-/h^+ pair chemistry of semiconducting metal oxide (MO) materials by examining the influence of surface structure, defects and dopants on the photocatalytic activity of narrow bandgap materials (TiO_2) An outcome of this proposed work will be a more thorough evaluation of the use of ionizing radiation in the catalytic remediation of organics (and other problem species) in high-level mixed waste.

Research Progress and Implications

We have observed that the yield of γ–ray induced destruction of EDTA in solution increased significantly if oxygen and a colloidal suspension of TiO_2 were present. Both oxygen and TiO_2 were necessary to see this increased EDTA destruction. Without TiO_2, about 19% of the EDTA in an aerated solution was destroyed after a 1 MRad γ–ray exposure, but with a 0.1 g/ml suspension of TiO_2 the level of EDTA destruction increased to near 50%. However, this process is very pH dependent. As the pH is increased the difference between the blank experiment (no TiO_2 present) and that with TiO_2 present becomes zero. This implies that as the pH increases the surface charge on each TiO_2 particle becomes increasingly negative, and anionic species, such as EDTA, are unable to directly interact with the surface. This effect is overcome if EDTA is complexed with a cation such as Sr^{2+}. At a pH of 9 the level of EDTA destruction is approximately the same after a 1 MRad exposure with or without TiO_2. If the solution is made with 0.2 M in Sr^{2+} the level of EDTA destruction increases to about 25% after a 1 MRad exposure, while a 0.12 M solution increases the level to over 30%. We interpret this to mean that complexed EDTA is an electrostatically neutral solution species and is therefore insensitive to the negative charge on a TiO_2 particle at high pH. We have also observed that Cu^{2+} ions produce the same effect as Sr^{2+}, which is consistent with EDTA complexing with 2+ cations in general. This finding has great significance for the radio- and photo-catalytic destruction of complexants such as EDTA because pH effects can be negated. The effect is minimal at a pH of 5, where the surface charge on TiO_2 is close to zero. These results are also consistent with UV photoxidation studies conducted by Prof. Dayte's group at the University of New Mexico.

We have also undertaken to characterize the solution and gas phase products from radiocatalytic destruction of EDTA over TiO_2. Although several products are observed from solution radiolysis in the absence of TiO_2, there is a significance increase in the yields of ED3A and formic acid, as well as a decrease in the yield of oxalic acid, when TiO_2 is present. Assuming that charge transfer occuring between the γ–ray excited TiO_2 surface and the adsorbed EDTA species is responsible for EDTA decomposition, we expect that the anchoring group of the molecule is most susceptible to TiO_2-mediated oxidation. Based on comparisons with the binding of carboxylic acids, such as formic acid and acetic acid, to TiO_2, we expect that EDTA should bind to the surface through only one of its four carboxyl groups due to steric issues. Therefore, the production of ED3A is consistent with this model in that one acetate moiety is preferentially decomposed per EDTA molecule destroyed.

Because formic acid was one of the major product of EDTA radiocatalysis and because we wish to better understand the mechanism of radiocatalysis, we have undertaken studies aimed at smaller probe molecules. Our initial results indicate that formic acid, acetic acid and ethanol are all insensitive

to the presence of TiO_2 in the γ–ray experiments, that is, the extents of γ–ray radiolysis are the same for these molecules in solution regardless of the presence of TiO_2. This result for formic acid is consistent with the EDTA experiments that show a gradual evolution of this species with increasing radiation dose implying that formic acid accumulates in solution without being further decomposed. However, this result is also surprising because UV photolysis conducted by us and in several published accounts indicate that small organics such as formic acid are rapidly photoxidized over TiO_2.

Although we do not yet understand the absence of γ–ray induced radiocatalytic destruction of these small organics, we have observed that impregnating TiO_2 with 0.5% Pt increases the rate of formic acid decomposition threefold over that of solution radiolysis. We believe this is a thermal effect because the yields of CO_2 produced are equivalent irrespective of the presence of γ–ray irradiation. During these γ–ray irradiation experiments we also observed significant yields of hydrogen gas that were not observed without platinized TiO_2 present or without irradiation. This hydrogen did not arise from photoreduction of water on the platinized TiO_2 since identical experiments in the absence of formic acid did not yield H_2.

In an effort to determine the role that various excitation mechanisms play in the γ–ray experiments over TiO_2, we have conducted controlled experiments with small organic molecules over TiO_2 single crystal surfaces in ultrahigh vacuum (UHV). One possible mechanism that might occur in solution is the effect of secondary electron induced chemistry resulting from absorption of the high energy radiation. For example, a Compton electron, formed by absorption of a γ–ray, can produce up to 10^4 100 eV electrons through subsequent ionization and loss processes. These electrons should be very effect at breaking bonds. In order to determine the cross sections, and thus the relative rates, for electron-induced decomposition of small organics on TiO_2, we conducted a series of experiments focusing on the 100 eV electron irradiation of methanol on TiO_2(110). These experiments were done in collaboration with Prof. Miguel Castro from the University of Puerto Rico. Methanol was chosen as the organic probe molecule for these experiments because it is the simplest organic that has no thermal decomposition on TiO_2(110). Molecularly adsorbed methanol on the TiO_2(110) surface left no detectable carbon-containing fragments after irradiation with 100 eV electrons. In contrast, electron irradiation of methoxyl species resulted in adsorbed formaldehyde.

The cross section for 100 eV electron induced decomposition of molecularly adsorbed methanol was 1.7×10^{-16} cm^2 (only a factor of 2.5 less than that for the gas phase). This indicates that the TiO_2(110) surface does not quench the excited states of methanol resulting from electron impact ionization. The cross sections for methoxyl decomposition was about 5×10^{-16} cm^2. These large cross sections suggest that small organics like methanol should readily decompose on TiO_2 surfaces exposured to 100 eV electrons, it does not appear that the γ–ray studies show the same type of reactivity. This suggests that secondary electrons with energies above the ionization potentials of most organics (above 10 to 20 eV) are not generated in significant concentrations when TiO_2 suspension are irradiation with γ-rays. The chemistry associated with less than 10 eV electrons has not been examined by our group, but is planned for the next year of this project.

Planned Activities

We will focus on the following areas in the next year:

We will continue studies aimed at determining the mechanism of the γ–ray radiocatalysis effect over TiO_2. These will include more studies involving small probe molecules, but also expanding into the area of photoreduction of metals. This effort will include looking at new TiO_2-based materials such as 10Å wide particles of anatase obtained from Dupont, and mesoporous materials grown in-house by Scott Elder.

We will begin work on ZrO_2. This will include growth of model ZrO_2 materials by molecular beam epitaxy that will be used to probe the photodynamics and charge carrier properties of wider bandgap materials.

We will continue probing the role of oxygen vacancies and reactive oxygen species in the photoxidation of organics over single crystal TiO_2 substrates. For example, we will further probe the oxidation of N_2 with oxygen adatoms and expand this work to consider organics such as acetone and propylene.

We will explore the ability of low energy (below 10 eV) electrons to activate adsorbed molecules, such as methanol, on the surface of TiO_2(110).

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Stability of High-Level Waste Forms

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Research Objective

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

Research Progress and Implications

This report summarizes work after 8 months of a 3-year project. Initial efforts in the project involved further information gathering and the updating of software. Reports on earlier thermochemical efforts supported by Pacific Northwest National Laboratory (PNNL) were acquired. Site visits to PNNL related to activities in the Tank Focus Area were used to obtain information on important waste glass issues.

The ChemSage software was upgraded to version 4.0 which allows for more efficient file handling and provides interfaces with Lotus and Excel spreadsheets. Identical software was provided to all program participants so that the interchange of calculations are facilitated.

The subsystems which make up the host glass system need to be initially modeled. Utilizing the database associated with the ChemSage software, and after necessary modification, the phase equilibria of the systems Na_2O-SiO_2, Al_2O_3-SiO_2, Na_2O-Al_2O_3, and Li_2O-Al_2O_3 were evaluated. The associated species model was used such that all the phases formed from combinations of the metal oxides were assumed to exist in a single, ideal solution phase. This phase is thus the glass phase. The thermochemistry requires that heats for fusion be added to the 298 K enthalpy of formation and the entropy adjusted by adding the heat of fusion divided by the melting point to the 298 K entropy. Thus the phase is treated as a liquid below its melting point.

The associated species model for the glass phase was used in equilibrium calculations for the above phase systems in order to reproduce their reported phase diagrams. The ability to reproduce the phase diagram is an indication of the appropriateness of the model since the phase equilibria are typically very sensitive to thermochemical values. Not surprisingly, some modifications to the thermochemical values of the solution species were necessary in order to reasonably reproduce the phase diagrams. For the Na_2O-SiO_2 making the 298 K enthalpy of formation for the $Na_2Si_2O_5$

solution species 10 kJ more positive allowed for an excellent match with the experimentally-determined phase diagram.

Planned Activities

Experiments required to determine melting points of urania-boria compositions have been initiated. This data is key to accurate modeling of borosilicate glasses containing actinides, and is not available in the literature. This work should be completed by September 1998. A system for assembling the binary oxide phase equilibria into the multicomponent database necessary for the global compositions is being developed, and should also be completed by the end of the fiscal year. Simultaneous with that is the modeling of the lithia-containing binary oxide systems.

Fiscal 1999 will be devoted to completing the subsystem database, incorporating the urania-boria data, and performing other necessary urania experiments. It is expected that the first global glass activity computations will be performed before the end of the fiscal 1999. The final year of the program will see global calculations performed on a number of practical glass compositions and the results compared to available activity/solubility data. Initial efforts will be made to use similar techniques for spent nuclear fuel to assess the feasibility of the approach.

New Silicotitanate Waste Forms: Development and Characterization

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Research Objective

The objective of this program is to identify new waste forms and disposal strategies specific to crystalline silicotitanate (CST) secondary waste that is generated from Cs and Sr ion exchange processes. In particular, in-situ heat treatment of CSTs to produce an alternate waste form is being examined. Waste forms that are developed in this work will offer an alternative to current disposal plans which call for recombining the separated Cs, Sr-loaded CST into the high activity waste streams then dissolving it in borosilicate glass. The goals of the program are to reduce the costs associated with CST waste disposal, to minimize the risk of contamination to the environment during CST processing, and to provide DOE with technical alternatives for CST disposal. Because there is uncertainty in repository availability and in waste acceptance criteria, it is likely that Cs and Sr loaded ion exchangers will require short term storage at Hanford or that new scenarios for long term storage or disposal of nuclides with relatively short half lives (such as ^{137}Cs and ^{90}Sr) will arise. Research activities in this program will generate information on the durabilities and stabilities of thermally consolidated CSTs so that the potential of these options as viable storage or disposal scenarios can be evaluated. The technical objectives of the proposed work are to fully characterize the phase relationships, structures and thermodynamic and kinetic stabilities of crystalline silicotitanate waste forms and to establish a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry.

Research Progress and Implications

This report summarizes work after seven months of a three year program. To date studies have been performed to: 1.) determine the durability of waste forms synthesized by heat treating the UOP CST IE-911, 2.) investigate the stable and metastable phase formation from heat treated CST and from model 3-component systems, and 3.) measure the heat of formation for the CST without proprietary components. Leach tests have shown that waste forms with durabilities orders of magnitude higher than baseline borosilicate glass can be achieved by a simple heat treatment of the Cs-loaded ion exchanger with no additives. Optimum durabilities are achieved at heat treatment temperatures in the range of 800-1000°C. Direct thermal conversion reduces the total volume of waste generated from the ion exchanger by about 40% and dramatically simplifies processing. In addition, heat treatment of the ion exchanger coarsens fines, reducing inhalation risk, and completely removes molecular water and hydroxyl groups, eliminating the possibility of radiolytic hydrogen production during storage. The IE-911 CST ion-exchanger is compositionally complex. There are a number of phases that appear when the ion exchanger is heat treated, several of which are new. After heat treatment between 800-1000°C (where the best durability is obtained), a mixture of crystalline phases precipitates that are different from the structure of the ion exchanger. Preliminary NMR and x-ray diffraction simulation results indicate that the Cs resides in solid solution in a crystalline sodium titanate. Phase equilibria and single crystal growth experiments on the three component Cs_2O-TiO_2-SiO_2 system have revealed two new stable compounds. One of these compounds is related to a silicotitanate pollucite compound discovered at PNNL that encapsulates Cs in a covalently bonded silicotitanate cage. In addition, two new (potentially metastable) phases have been synthesized in the Cs_2O-TiO_2-SiO_2 system using hydrothermal techniques.

Planned Activities

Future work will concentrate on identifying all Cs-containing phases in the heat treated waste forms and determining their thermodynamic stabilities so that long term predictions of durability can be made. A solid solution series of (Cs,Na) $^2Ti_6O_{13}$ compounds will be synthesized for analysis by X-ray diffraction, NMR, and solution drop calorimetry. The stability of Cs-containing compounds when it radioactively decays to Barium-137 is of concern. When Cs-containing phases have been identified and characterized, solid solutions such as (Ba, Cs, Na) $^2Ti_6O_{13}$ will be synthesized and analyzed for stability, chemical durability, crystal structure type and Cs environment. Crystal growth studies revealed that there is a tetragonal phase with composition near the cubic pollucite phase. Diffraction and DSC studies will be performed on this phase to determine if there is a low temperature cubic to tetragonal transition. Variations in reaction conditions will be attempted in order to synthesize phase pure samples for XRD and thermochemical analysis.

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Ion-Exchange Processes and Mechanisms in Glasses

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Research Objective

Recent performance assessment calculations of a disposal system at the Hanford Site in Washington State for low-activity waste glass show that a sodium ion exchange reaction can effectively increase the radionuclide release rate by over a factor of 1000. The susceptibility of the glass to alkali ion exchange is thus a major factor limiting waste loading. However, low temperature ion exchange has not been thought to be important in recent analyses of waste glass durability. The objective of this work is to develop an understanding of the processes and mechanisms controlling alkali ion exchange and to correlate the kinetics of the ion exchange reaction with glass structural properties. The fundamental understanding of the ion exchange process developed under this study is targeted at developing lower ion-exchange rate glasses that would remain durable at higher alkali waste loading.

Research Progress and Implications

This report summarizes eight months of work on this three-year project that is being performed cooperatively between Pacific Northwest National Laboratory and Lawrence Berkeley National Laboratory. A Series I set of glasses in the system Na_2O-Al_2O_3-SiO_2 was developed; the objective was to vary the distribution of Na^+ among Q3Si non-bridging oxygen (NBO) and four-coordinated Al sites. A base glass of $33.33Na_2O$-$66.67SiO_2$ (in mol%) was selected because this formulation contains the largest amount of Na_2O possible to theoretically maintain no more than one NBO per Si atom. Five Na_2O-Al_2O_3-SiO_2 glasses were formulated, with the concentration of Al_2O_3 ranging from 0 to 20 mol%.

Samples of these glasses, as well as reference materials, were analyzed using 27Al solid-state nuclear magnetic resonance (NMR). The results showed only a single, broad, asymmetric 27Al NMR peak at 61±1 ppm. A peak at this position indicates tetrahedrally coordinated Al rather than octahedrally coordinated Al, confirming that all of the Al in these glasses occurs as tetrahedrally coordinated network forming sites, presumably by association with charge-compensating Na^+ ions. Substituting Al_2O_3 for SiO_2 also shifts the ^{29}Si NMR peak position systematically as the Al_2O_3 content of the glass increases. This indicates that the Na^+ is transferred from being associated with Q3Si sites to being associated with network-forming Al sites, which will presumably affect the rate of Na^+ ion exchange.

Additional structural characterization of these glasses was carried out using a new experimental approach to obtain x-ray absorption fine structure (XAFS) data from the Na K-edge using the high photon energy capabilities of a spherical grating monochromator matched with an undulator source at the Advanced Light Source (ALS). To the best of our knowledge, these are the first studies to take advantage of these new opportunities. Smoothed Na XAFS spectra were collected at the ALS in fluorescence detection mode from the test glasses and a reference material. Differences were clearly observed in the near-edge region of the spectra. The data from the extended portion of the Na XAFS spectra are being processed and theoretically fit to determine whether they are of high enough quality to permit the extraction of the Na structural parameters. The results of these studies firmly substantiate that XAFS of glass constituents will provide the structural information component necessary to understand the role of Na in the ion exchange process and many other light element interactions in glasses as well. This speciation knowledge is difficult to obtain directly, and XAFS provides a means to do so, even in glasses that contain a full complement of paramagnetic constituents.

An accurate measurement of the rate of Na ion exchange from the test glasses is another key challenge on this project. The experiments must be performed under controlled conditions of constant pH, temperature and solution composition. To accomplish this, a flow-through experimental design was selected. However, numerous design challenges had to be overcome: 1) glass coupons must be used to provide samples for surface layer depth profiling, 2) several coupons must be exposed to the leachant solution simultaneously to provide a time sequence set of samples for analysis, and 3) fluid volumes need to be minimized because $D_2{}^{18}O$, which is expensive, will be used in some tests. The flow-through reactor design we developed to meet these challenges employs a single pass flow through column and contains five compartments or "cells" to hold individual glass coupons. Each cell is independently accessible by removing its stainless steel cover and Teflon seal. Although flow-through testing has just begun, the results from a test with the 15 mol% Al_2O_3 glass in a pH 8 silicate buffer solution showed that the Na concentrations approach a steady-state concentration, which is the goal of this test design. Sodium release rates for this glass were about 3 orders of magnitude faster than the long-term ion exchange rate we have measured in static tests on typical low-activity waste (LAW) glasses at this same temperature. We believe this is because the pH is 2 to 3 units lower in this flow-through test than in the static tests. Ion exchange rates are expected to be a strong function of pH, so rates in the pH 8 flow-through experiments are expected to be higher. These simple three-component glasses are also likely to be more susceptible to ion exchange reactions than real multicomponent LAW glasses.

Trial tests were also performed on the isotope-specific surface spectroscopies that will be used to characterize distribution of labeled water species in hydrated glass surface layers. These measurements were made using a Van de Graaff accelerator and nuclear reactions D(d,p) ^3He, ^{18}O (p, alpha) ^{15}N for deuterium and oxygen analysis. The 10 and 15 mol% Al_2O_3 glasses were exposed to 30 mL of water made up from 10 mL of ($D_2{}^{18}O$ - 97.46 at% ^{18}O and 76.4% D) and 20 mL of ($D_2{}^{16}O$ 99% D). Both glasses showed a considerable amount of deuterium uptake with the penetration depth for the 10-mol% Al_2O_3 glass significantly greater than that of the 15-mol% Al_2O_3 glass. These results are consistent with the expected differences in durability of these glasses. We conclude from these preliminary results that the nuclear reaction analysis technique appears to be viable for studying D and O uptake in these glasses.

Planned Activities

A second series of glasses will be developed incorporating B_2O_3 to further test glass structure/property correlations. Flow-through experiments in H_2O and D_2O are in progress on the Series I glasses and most will be completed by fiscal year end, as will the tests in $D_2{}^{18}O$. Experimental, theoretical, and data processing activities related the Na K-edge XAFS investigations are critical activities. The results of these Na investigations, the theoretical simulations, and the quality of the structural parameters obtained will determine the approach used for characterizing Na environments for the duration of the project. At the same time, the B K-edge will be investigated by both total yield and fluorescence detection methods to compare B coordination environments from the near surface region and the bulk. This will be done with glasses that have had the B coordination previously examined by NMR.

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

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Research Objective

The research objective was to test and develop optical methods for real-time, remote and in-situ testing of corrosion processes on the surface of vitrified nuclear wastes.

Research Progress and Implications

This report summarizes the research conducted in the first 1.5 years of a 3 year grant. At this point, we have identified the conditions for optimal tests and demonstrated that both IR reflection and Raman spectroscopies can be used to determine the dealkalization process in the surface of simple glasses in real time.

Research Progress

Simple, model silicate glasses containing one and two alkali (Li and Na) oxides were melted and cut into small blocks and the surfaces polished. The blocks were then subjected to static leach tests in deionized water with a surface to volume ratio of 0.1 cm^{-1}. Bath temperatures were varied between 20 and 100°C. Drip tests were also conducted in which de-ionized water flowed at a rate of 0.01 ml/min over the surface (3 cm^2) of one side of the samples. The samples consisted of glasses with low chemical durability, selected to enhance the surface dealkalization process and allow it to develop in a short time period. They were 20%Na_2O-80%SiO_2, 20%Li_2O-80%SiO_2, 7%Na_2O-7%Li_2O-86%SiO_2, and several simulated SRL waste glasses.

Both static leach test and drip test samples were examined after various lengths of exposure by two methods: reflection FTIR spectroscopy and reflection Raman spectroscopy. In the FTIR tests, samples were removed from the bath, were dried and measured. In the Raman tests, samples were measured in-situ without removal from the bath. Both tests showed the expected peaks (corresponding to IR absorption in the FTIR tests, and shifted emission in the Raman tests) typically observed in these materials in the ranges of 400-600 cm^{-1}, 800 cm^{-1} and 1000-1200 cm^{-1}. It was interesting to note that the indicative changes in peak intensities with an alteration of the surface composition consisting of loss of alkali were most obvious in the 400-600 cm^{-1} range for the Raman tests and in the range 1000-1200 cm^{-1} in the FTIR tests.

The FTIR tests consist of measurements of the reflection coefficient of the corroded surface. In these tests, we examined the peaks resulting from absorption processes between 600 and 1200 cm^{-1}. These correspond to the bending or asymmetric stretch vibrations of the O-Si-O and the R-O-Si structures in the glass. Theses peaks have been observed to change with exposure to water in previous studies, however no quantitative analyses were conducted. In past studies, the peaks were observed to shift and change in intensity with leaching, thus defeating any attempt at quantifying the degree of leaching or dealkalization. In the present study, we modeled the FTIR reflection spectra using 5 Gaussian absortion peaks. There peaks were added to form an extinction coefficient and the corresponding wavelength-dependent refractive index was calculated using Kramers-Kronig calculations. The modeled reflection spectra were then fitted to the measured spectra by allowing peak position, peak intensity and peak width to vary. Our results showed an excellent fit of the data with our modelled absorption peaks. It is important to note that using this more appropriate analysis,

the pead positions and peak widths varied very little as a result of leaching of the glass surface. Only the peak integrated areas showed considerable changes with degree of de-alkalization.

Analysis of the Na_2O-SiO_2 glass showed a marked decrease in intensity of the Na-O-Si vibration at 990 cm-1 with dealkalization of the surface, and a marked increase in intensity of the O-Si-O vibration at 1110 cm-1. The time dependence of these intensity changes is currently under analysis to determine if it can be directly correlated (quantitatively) to the amount of surface dealkalization. Studies on the other glasses are slower due to their better chemical durability, but the results are essentially identical. In the Li_2O-SiO_2 glass, the same behavior is observed for the O-Si-O peak, while the Li-O-Si peak is obseved at 910 cm^{-1}. In the Li_2O-Na_2O-SiO_2 glass, the alkali peak occurs at 950 cm^{-1} and corresponds to a mixed alkali vibration.

Raman measurements were conducted on similar samples, except that the tests were all conducted in-situ, without removal of the samples from the leaching bath. At this time, we can only give preliminary results because of an unexpected problem that arose from the setup in the Raman tests which prevents isolating the Raman signal scattered from the sample surface. Consequently, signals scattered from the bulk of the sample were also present and often masked the surface signal. When the surface signal dominates, we have been able to observe variations in intensity in two peaks (470 and 580 cm^{-1}) in the Li_2O-SiO_2 glass. The variations are less well-defined than the FTIR peaks, but they clearly indicate de-alkalization.

Implications

Two complementary techniques were used to follow surface dealkalization changes in model silicate and borosilicate glasses: FTIR and Raman spectroscopies. FTIR examines the infrared absorption behavior of the material. Because glass samples strongly absorb IR signals, this is a surface sensitive method, generally limited to a depth of less than a few hundred nanometers. By development of a novel method for analysis of the FTIR data, we have demonstrated that the FTIR method has a potential for a quantitative measure of the glass surface condition, especially de-alkalization and have identified the peaks of principal importance. Further tests will examine the formation of precipitates on the surface. The FTIR method however is limited to observation of relatively dry surfaces since the IR signal is also strongly absorbed by water. Consequently, it cannot be used on submerged samples.

In contrast, the Raman method uses visible light and therefore can be used on submerged samples. In our tests on simple glasses, we have discovered that the geometry of the test is critical because the visible light also penetrates the transparent glass samples and it is difficult to extract surface data from the measurement. However, this problem disappears in simulated, waste-containing samples since they are not transparent. In that case, the tested region of the sample becomes limited to the surface. Preliminary tests show that the Raman approach has great promise for the examination of non-transparent samples whether submerged or not.

Planned Activities

Planned activities include:

(1) tests to determine the accuracy of the measurement of surface de-alkalization by FTIR,
(2) a continuation of FTIR studies in more complex glasses,
(3) Raman studies in iron-containing glasses to isolate the active region to the sample surface,
(4) an analysis of the quatitative value of Raman tests,
(5) extension of studies to the formation of surface precipitates, and
(6) coordinated Raman and FTIR tests on simulated waste glasses to determine important peaks that relate to the surface chemistry of the materials.

The FTIR tests on model glasses will be completed and analyzed by the end of the second year. The Raman tests on model glasses will be conducted into the first quarter of the third year. The third year will be spent in testing simulated-waste-containing glasses.

Mixing Processes in High-Level Waste Tanks

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Research Objective

Flammable gases can be generated in DOE high-level waste tanks, including radiolytic hydrogen, and during cesium precipitation from salt solutions, benzene. Under normal operating conditions the potential for deflagration or detonation from these gases is precluded by purging and ventilation systems, which remove the flammable gases and maintain a well-mixed condition in the tanks. Upon failure of the ventilation system, due to seismic or other events, however, it has proven more difficult to make strong arguments for well-mixed conditions, due to the potential for density-induced stratification which can potentially sequester fuel or oxidizer at concentrations significantly higher than average. This has complicated the task of defining the safety basis for tank operation.

Waste-tank mixing processes have considerable overlap with similar large-enclosure mixing processes that occur in enclosure fires and nuclear reactor containments. Significant differences also exist, so that modeling techniques that have been developed previously can not be directly applied to waste tanks. In particular, mixing of air introduced through tank roof penetrations by buoyancy and pressure driven exchange flows, mixed convection induced by an injected high-velocity purge jet interacting with buoyancy driven flow, and onset and breakdown of stable stratification under the influence of an injected jet have not been adequately studied but are important in assessing the potential for accumulation of high-concentration pockets of fuel and oxygen. Treating these phenomena requires a combination of experiments and the development of new, more general computational models than those that have been developed for enclosure fires.

Research Progress and Implications

U.C. Berkeley is now completing the second year of its three-year project that started in September, 1996. We made excellent progress in several important areas related to waste-tank ventilation and mixing processes.

Ceiling Air Ingress: In the first area, we completed a series of experiments using salt-water solutions to simulate buoyancy-driven flows through openings in horizontal partitions. This provides one of the major mechanisms for the entry of air through ceiling ports into inerted waste tanks following loss of ventilation, due to the density difference of the warm gas inside the tank and the cooler gas outside. We developed a laser-based diagnostic technique for measuring the transient evolution of the vertical density distribution in the experiment [1], providing data to bench mark the numerical mixing models now under development. The most interesting result of the experiments was the discovery that previous experiments by other investigators had incorrectly measured transient density evolution, requiring an empirical correction to the simplest fundamental models for the exchange flow rates [2]. With the new diagnostic method developed under this research effort, we were able to show that the transient flow rates closely follow the simple model, lending confidence to calculations that have been performed to predict the rate of air ingress into inerted waste tanks following loss of ventilation.

Mixed Convection from High-Velocity Purge Jets: Mass transfer from the liquid surface in high-level waste tanks, which controls the distribution of flammable gases, is driven by a combination of natural convection from the warm liquid to the cooler gas space, and potentially by forced convection if a high-velocity gas jet is injected, as is done for inerted tanks. We recently made new observations, based on limited data on jet-induced heat transfer available in the chemical engineering literature, that indicates that relatively simple correlations should be possible to predict the combined effects of forced and natural convection in waste tanks [3]. We are currently finishing assembly of

a scaled waste-tank system to study this mixed convection problem for heat and mass transfer from a horizontal, upward facing heated surface in a cylindrical enclosure, with scaled purge jet injection.

Modeling for Transient Density Evolution: When one attempts to numerically solve the multi-dimensional mass, momentum, and energy equations with CFD codes, very fine grid resolution is required to resolve these thin jet structures, yet such fine grid resolution is difficult or impossible to provide due to computational expense. However, we have shown that the ambient fluid between jets tends to organize into either a homogeneously mixed condition or a vertically stratified condition that can be described by a one-dimensional temperature and concentration distribution. Furthermore, we can predict the transition between the well-mixed and stratified conditions. This allows us to describe mixing processes in large, complex enclosures using one-dimensional differential equations, with transport in free and wall jets modeled using standard integral techniques. With this goal in mind, we are constructing a simple, computationally efficient numerical tool. The tool has been benchmarked against analytical solutions for idealized mixing conditions, showing that the numerical truncation errors are quite small, and will be benchmarked against experimental data over the next year.

1. C.J. Lee, S.Z. Kuhn, and P.F. Peterson, "Measurement of the Transient Evolution of Density in Stratified Liquid Enclosure Experiments," in preparation for submission to Experimental Heat Transfer.
2. S.Z. Kuhn, J. Christensen, C.J. Lee, and P.F. Peterson, "Enclosure Mixing Induced by Buoyancy-Driven Exchange Flows in Horizontal Partitions," in preparation for submission to Journal of Heat Transfer.
3. P.F. Peterson and R.E. Gamble, "Scaling for Forced-Convection Augmentation of Heat and Mass Transfer in Large Enclosures by Injected Jets," submitted to the ANS Summer Meeting, Nashville, TN, June 7-11, 1998.

Planned Activities

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

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

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Charles Crawford, Westinghouse Savannah River Company
James Ritter, University of South Carolina
Sheldon Landsberger, University of Texas

Research Objective

The objective is to reduce the volume and cost of high-level waste glass produced during U.S. DOE remediation activities by demonstrating that magnetic separation can separate crystalline, amorphous,

and colloidal constituents in vitrification feed streams known to be deleterious to the production of borosilicate glass. Magnetic separation will add neither chemicals nor generate secondary wastestreams. The project includes the systematic study of magnetic interactions of waste constituents under controlled physical and chemical conditions (e.g., hydration, oxidation, temperature) to identify mechanisms that control the magneticproperties. Partitioning of radionuclides to determine their sorption mechanisms is also being studied. The identification of fundamental magnetic propertieswithin the microscopic chemical environment in combination with hydrodynamic and electrodynamic models provides insights into the design of a system for optimal separation. Following this, experimental studies using superconducting open-gradient magnetic separation (OGMS) will be conducted to validate its effectiveness as a pretreatment technique.

Research Progress and Implications

The team working on this project includes Argonne National Laboratory, Westinghouse Savannah River Technical Center (SRTC), the University of South Carolina (USC), and University of Texas (originally University of Illinois.)

As of October 1997, a drum of Hanford C-103 sludge which has a high Fe concentration and hence should be amenable to magnetic separation, SRTC flyash, and a Pu-flyash from Rocky Flats were sampled and studied by SEM. Initial chemical characterization by SRTC was augmented with investigations of mineral composition and magnetic susceptibility using a SQUID magnetometer. Interestingly, the Hanford C-103 sludge magnetic susceptibility shows a strong temperature dependence while the flyash showed virtually no temperature response. In addition, the flyash contains many particles in the sub-micron range which present significant material handling challenges for a pre-treatment system. All this suggests that Hanford C-103 sludge will be the candidate for initial detailed engineering studies.

Engineering considerations for magnetic separation require that an optimal system screen the highest susceptibility materials using a high-gradient magnetic separation (HGMS) system. As of April 1998, these initial screening studies have been concluded at USC. They suggest that considerable beneficiation for the Hanford C-103 sludge can take place using conventional HGMS. Silica, gibbsite, and boehmite were present in considerable amounts and apparently served as nucleationor coordination sites for Fe.

As of April 1998, considerable progress was made in adapting two modeling programs to support the engineering of an OGMS system at Argonne. In both of these cases, the simplest case of a free-fall system was investigated. The first of these models follows only the trajectory of a single particle passing through an OGMS system. Results from this model relate the initial radial position free-falling through the vertical bore of a superconducting quadrupole field with a 70 cmlength superconducting magnet having a maximum gradient of 60 T/m will be sufficient to effect the magnetic beneficiation of even paramagnetic fractions. Particle size will have a considerable impact on trajectory with the optimal size being 50-100 microns.

As of April 1998, a multi-particle simulation at Argonne based on ICRKFLO also has been developed. This builds on work currently being conducted for the EPA to beneficiate petroleum cracking catalysts which are comprised of paramagnetic kaolin and zeolite spherical paticles around 50 microns in diameter. Results from the ICRKFLO work suggest that care must be taken to introduce the particles so as not to introduce excessive dispersion by minimizing the spray angle. Assuming plutonium oxide particles were in the feed, the study showed that they would be effectively captured by the OGMS.

Planned Activities

Tests of the Open-Gradient Magnetic Separation will be conducted during the fourth quarter FY98 to establish operating conditions for these feeds and provide date for model validation. Initial preparation for the neutron activation analysis studies at UT has taken place, and further progress is expected during third and fourth quarter FY98.

Other Access To Information

Nunez, L., R.D. Doctor, M.D. Kaminski, and A.E. Visser, "Superconducting Open-Gradient Magnetic Separation for the Pre-treatment of Radioactive or Mixed-Waste Vitrification Feeds," Tenth Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN (October 20-24, 1997).

Ebner, A., J.A. Ritter, and L. Nunez, "High Gradient Magnetic Separation for theTreatment of High Level Radioactive Waste," Separation Science and Technology, (accepted for publication.)

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

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Research Objective

This project seeks to develop an on-line sensor to measure the viscosity of dense slurries.

Research Progress and Implications

This report summarizes work after two years of a three year project.

The flow behavior of slurries is important for many of the proposed unit operations to be used in the conveying and processing of tank wastes. One alternative for determining the rheological properties of such materials is to obtain samples and test them off-line using conventional rheometers. Such a protocol is not practical for a wide variety of wastes. Rather, it is the goal of this work to find on-line, in - process techniques for measurement. There are two systems that we have propose examining: (1) Nuclear magnetic resonance imaging (NMRI), and, (2) Ultrasonic Doppler Velocimetry. Central to both of these techniques is the measurement of velocity profiles in pipe flows.

For the NMRI measurements, the presence of particles has two principal effects on the NMRI velocity profiles: a decrease in signal intensity and image blurring. Similar effects are observed in turbulent flows due to the local random fluctuations in the flow. This similarity has led us to turbulent flow using NMRI. The governing equations for the signal obtained by NMRI are the Bloch-Torrey equations. Previously, we showed a relationship between turbulent fluctuations and spatial signal intensity variations, assuming isotropic turbulence. However, this assumption does not reflect the true nature of turbulence in a pipe flow where the turbulence is not isotropic. In our new work the Bloch-Torrey equations will be solved by first, time averaging and then employing a turbulence model for pipe flow. The purpose of the time averaging is to smooth the fluctuations of time scale smaller than that of NMRI data acquisition.

After this work with single phase fluids, we shall undertake NMRI experiments of slurry flow. Various operational parameters will be optimized during the experiments to obtain velocity profile of the flow. Pressure drops will also be recorded to obtain shear stress distribution. Plot of shear stress versus the shear rate, obtained from the velocity profile, will yield the shear viscosity over a wide range of shear rate. The velocity images will also be analyzed to compare the effects of fluctuations with those of turbulent flow experiments

For single phase fluids, the NMRI and the UDV work will be compared with measurements using LAV. In our LAV. flow apparatus, the working fluid, water, is gravity fed from a reservoir into a horizontal one inch Pyrex tube, 180 diameters in length. The system enables traverses of the optical probe in the horizontal and vertical directions, with a resolution of 200 micrometers.

Radial distributions of the axial component of velocity were obtained at a location 150 diameters from the tube entrance. Measurements in the laminar regime indicate a precision of within one percent, as indicated by the root mean square fluctuations. In the turbulent regime, radial profiles of the mean and fluctuation velocities agree with literature values. In the laminar regime, symmetry of the radial velocity distribution was observed in the horizontal plane passing through the axis, but was not in general observed in the vertical plane passing through the axis. Further investigation revealed that the asymmetry was a result of buoyancy due to heat transfer between the working fluid and the surroundings, even though the pipe was not actively heated or cooled. Temperature differences as little as 1 degree Celsius were found to result in significant asymmetry. To have a reproducible result in the laminar regime, it was necessary to control the reservoir temperature to within 0.1 degree Celsius.

Modeling efforts are underway to predict the asymmetric velocity profiles using a commercially available finite element code, FIDAP, which solves the Navier Stokes equations with the energy equation. Also, possible effects of this heat transfer phenomena on the transition to turbulence are being investigated.

The UDV work is aimed at the development and demonstration of a new approach for measurement of the velocity profile and local viscosity in a heterogeneous slurry pipe flow. This technique is based on simultaneous tomographic pulse-echo ultrasonic flow velocity and time-of-flight speed of sound measurements. Reconstruction of the velocity distribution is based on the measured local speed of sound, which depends on the local slurry concentration. To show the feasibility in applying this technique, we have carried out controlled experiments in the laboratory with known fluids and flow conditions. The two fluids tested were a viscous Newtonian fluid, propylene glycol, and a non-Newtonian fluid, Carbopol 980. The flow conditions tested were fully developed laminar pipe flow. The velocity measurements were validated against both LAV. measurements and theoretical predictions. The speed of sound results were shown to produce reproducible measurements and consistent with existing data. Obtaining an accurate velocity profile is our first milestone for developing an on line, real-time rheometer for measurements in dense slurries flowing within pipelines.

The experimental work with slurries is coupled with simulations of particle suspensions. Here, we have extended our previous studies of the mechanics of hydrodynamically interacting spherical particles having different sizes to suspensions of many sizes. Stokesian Dynamics is used to study the microrheology of suspensions having particles of two or more different sizes. The simulation is carried out by calculating the many body far-field hydrodynamic interactions, the near-field hydrodynamic lubrication resistances and the interparticle forces. Velocity and stress are then determined from these calculations, from which the position is integrated in time and the bulk suspension viscosity is found. Our work to date has shown that at fixed solids loading of particles, the relative viscosity of concentrated suspensions is lower when particles of different sizes are used than particles of the same size. This is illustrated by the case of suspensions including two sizes; the viscosity reduction increases as the ratio of the particle radii increases and it has a maximum reduction when about 25% of the particles (by volume) are of the smaller size. Our new studies include the effects of colloidal forces, particularly, DLVO forces and the effect of multiple sizes. The DLVO forces are electrostatic repulsion and van der Waals attraction. We have extended the scope of simulation to three dimensions involving Ewald summed periodic boundary conditions for polydisperse systems. The initial results show that the inclusion of the DLVO forces modifies the relative viscosity, with the effect increasing with ionic strength. For example, a bimodal suspension with size ratio of four to one and a relative volume fraction of 0.25 small spheres to large spheres demonstrates this behavior. The purely hydrodynamically induced relative viscosity, at 61.7% solids loading, is calculated to be 12.0, while the relative viscosity of a suspension of particles interacting electrostatically and via van der Waals forces (i.e. with a Debye length of 9.63nm) is calculated to be 18.6 (where the relative viscosity is the ratio of the viscosity of the suspension to that of the suspending medium). These calculations agree with literature data. Current work is aimed at quantifying these effects and understanding the role of the colloidal forces on the microstructure in concentrated suspensions of polydisperse particles.

Planned Activities

1. NMRI measurements in turbulent flow.
2. NMRI measuremnts with slurries.
3. UDV mesurments with slurries.
4. Simulations of polydisperse suspensions.

Acoustic Probe for Solid-Gas-Liquid Suspensions

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Research Objective

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

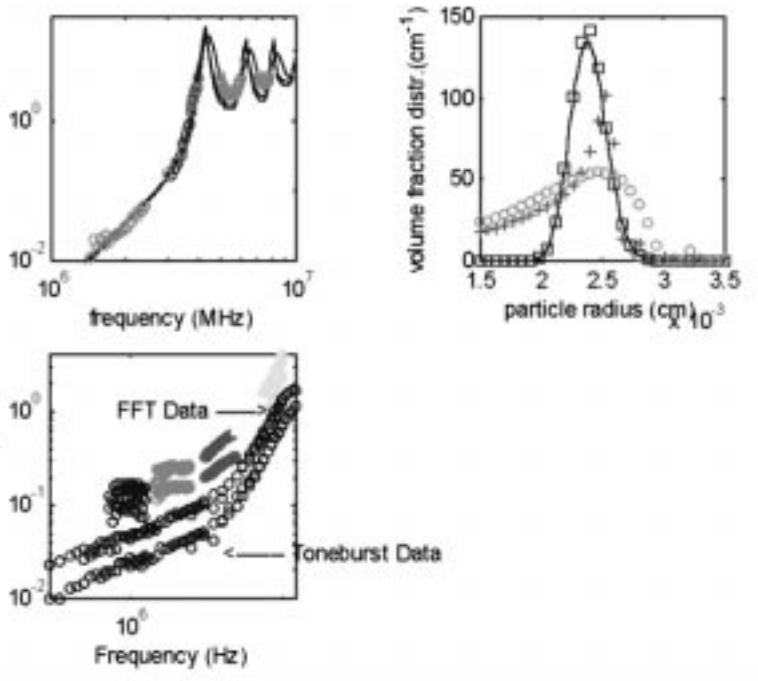
Research Progress and Implications

Theoretical Analysis Accomplished: As of October 1, 1997, conditions have been explored under which it is possible to determine the particle size distribution of a solid-liquid system from measurements on the attenuation of sound waves through the mixture. The attenuation in a polydisperse suspension can be written as follows:

$$\int v^*(a,\omega)\, \phi(a) da = v(\omega),$$

where $v^*(a,\omega)$ is the attenuation due to particles with radius a, and $\phi(a)$ is the volume fraction density, which is related to the particle size distribution. In the above equation to solve for the unknown $\phi(a)$, the right-hand side is known from experiments on a particular mixture, and $v^*(a,\omega)$ is known from theory. Such a problem is referred to as an 'inverse problem'. The theory used here for $v^*(a,\omega)$ is that of Allegra and Hawley (1972) for dilute suspensions of solids in liquid. This theory has been tested against experiments by solving a so-called 'forward problem': suppose we know the particle size distribution, what is the attenuation? Figure 1 shows very good agreement between the theory and experiments of the attenuation as a function of frequency for almost monodisperse polystyrene particles (radius 79μm).

In the past the inverse problem has been solved to determine bubble populations (Duraiswami 1993). Having used the same technique now for solids we have found that success is limited to very specific cases. Figure 2 shows that for the inverse problem to work for polystyrene particles it is necessary to have the attenuation over a suitable frequency range: the frequency range should include the wavelengths that are comparable to the particle size. However, it was not possible to solve the inverse problem for glass particles. This is explained by the differences in resonance behavior between glass and polystyrene particles.



Top, left (Figure 1): comparison between theory (lines) and experiments (markers); top, right (Figure 2): result for the particle size distribution when using different frequencies (Circles = 10 MHz, Crosses = 13 MHz, and Squares = 17 MHz) ; bottom, left (Figure 3): FFT and toneburst experimental data for different volume fractions.

*The implication of this result is that one **is not** able to solve the inverse problem to estimate the particle size distribution and volume fraction for solids in some cases.*

Experimental Work Accomplished: Extensive experimentation in solid-liquid systems has been carried out using the experimental setup described in the first year report. We have obtained attenuation data as a function of frequency in solid-liquid slurries of soda-lime glass beads (05-18.5 μm in radius, 9.5 μm mean) in water. Data have been obtained over the frequency range of about 0.5 to 12 MHz for slurries with concentrations ranging from 5 % to 30 % by volume, and these curves are shown in Figure 3. Attenuation data have also been obtained for a 5 % by volume slurry of 79 μm radius (essentially monodispersed) polystyrene spheres in water, and these results were compared with the forward solution in Figure 1. Additional attenuation measurements have been made in slurries of soda-lime glass beads (55-75 μm in radius, 64 μm mean) in a mixture of glycerol (29.7 wt %) and water. Measurements over the frequency range 1 to 7.5 MHz have also been made.

Fast Fourier Transform (FFT) analysis of received signals of spike pulse input signals has been tested and found to yield comparable results to those obtained by toneburst measurements, and is now the predominant data acquisition technique used in obtaining attenuation data.

Two sets of broadband transducers are being tested to replace the presently used five pairs of transducers for attenuation data acquisition from 1 to 10 MHz.

Planned Activities

The theory will be modified for non-dilute solid-liquid suspensions and the combined theory for gas-solid-liquid suspensions will be developed to determine the solids volume fraction in three phase slurries.

Attenuation measurements are also being attempted in bubbly liquids, and this work requires bubbles of desired properties. The most favorable method of bubble generation appears to be electrostatic spraying to generate bubbles in both the bubbly liquid and three phase experimentation.

The gas-solid-liquid theory will be compared to three phase attenuation data.

Other Access To Information

"Determination of Particle Size Distributions from Acoustic Wave Propagation Measurements", P.D.M. Spelt, M.A. Norato, A.S. Sangani, and L.L. Tavlarides. in preparation.

"Measurements in Solid-Liquid Slurries to Determine the Effects of Finite Solids Volume Fraction on Ultrasound Attenuation Behavior", M.A. Norato, P.D.M. Spelt, A.S. Sangani, M.S. Greenwood, and L.L. Tavlarides. in preparation.

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

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Research Objective

The objective of this project is to develop the scientific basis for hydrothermal separation of chromium from High Level Waste (HLW) sludges. Our worked is aimed at attaining a fundamental understanding of chromium speciation, oxidation/reduction and dissolution kinetics, reaction mechanisms, and transport properties under hydrothermal conditions in both simple and complex salt solutions that will ultimately lead to an efficient chromium leaching process.

Research Progress and Implications

This report summarizes our research over the first 1.5 years of a 3 year project. We have examined the dissolution of chromium hydroxide using different oxidants as a function of temperature and alkalinity. The results and possible applications to HLW sludges are discussed below.

Chromium hydroxide, $Cr(OH)^3\ ^3H_2O$ was selected as the first chromium compound for this study. Based on available literature, chromium hydroxide should be the majority chromium compound in the HLW sludges. Dissolution experiments on chromium hydroxide were conducted in two types of reactors: a stirred batch system and a continuous flow reactor. Liners of nickel or teflon were used to prevent corrosion or leaching of chromium from the reactors. Chromium hydroxide, i.e. $Cr(OH)^3\ ^3H_2O$, was prepared according to literature reports.

The two oxidants investigated were O_2 and nitrate. Dissolution/reaction experiments for chromium hydroxide in a batch reactor by O_2 were performed at reaction temperatures ranging from 75 to 200° C. The dissolution of chromium hydroxide using oxygen follows:

(1) When nitrate was used as an oxidant, the experiments were performed in both continuous flow and batch reactors at temperatures ranging from 250 to 410° C and pressures ranging from 300 to 4000 psi.

The reaction is:

(2) All experiments were performed in alkaline solutions from 0.01 to 4 M NaOH. A caustic environment was chosen because the Hanford waste is alkaline and neutralization is not practiced. Anions (CrO_{4-}^{2}, NO_{3-}, NO_{2-}) were measured by ion chromatography. Dissolution of chromium hydroxide under alkaline conditions with oxygen was studied at temperatures

ranging from 70 to 200° C. Hydroxide concentrations were varied from 0.01 to 4 M (pH 12 to 14.5) and oxygen concentrations in solution were varied from 0.4 to 4.4 mM to determine the effect of oxygen concentration and the caustic environment on the dissolution rates. The rate of oxidation to CrO_{4-}^{2} per 0.15 grams of $Cr(OH)^{3}$ $^{3}H_2O$ is:

(3) An increase in hydroxide concentration increased the dissolution rate with all other conditions being similar. The dependence was found to be almost linear, with a doubling of hydroxide concentration the dissolution rate nearly doubled. The oxygen concentration was determined based on the overall system pressure, partial pressure of oxygen and headspace volume. Henry's Law constants were used to determine the concentration of dissolved oxygen concentration in solution. An increase in oxygen concentration increased the dissolution rate but at a much lesser rate than the effect of hydroxide concentration. A four-fold increase in oxygen concentration was required to double the chromium dissolution rate. Temperature had the most significant effect on chromium dissolution with oxygen. Increasing the temperature 100° C (from 100 to 200° C) increased the rate nearly 150 times. The effects of chromium hydroxide surface morphology have not yet been determined.

Nitrate was used as an oxidant for dissolution of chromium at higher temperatures to 400° C. At reaction temperatures below 250° C, no dissolution of chromium was observed. At a nitrate concentration of 0.125 M, hydroxide concentration of 1.0 M and temperatures ranging from 250 to 400° C, the rate of oxidation to CrO_{4-}^{2} per 0.15 grams of $Cr(OH)^{3}$ $^{3}H_2O$ is:

(4) The diffusion and speciation of nitrate species at these conditions was also examined. The study of the effect of nitrate and hydroxide concentrations on chromium dissolution is in progress.

In conclusion, oxidative dissolution of chromium hydroxide can be accomplished at high temperatures with nitrate and at relatively low temperatures with molecular oxygen. We have determined the reaction rates for both systems. We have also determined diffusion constants and speciation of nitrates at releavent hydrothermal conditions. Our results suggest that at reaction temperatures (>125° C) slightly higher than the current baseline sludge washing conditions, chromium can rapidly and efficiently dissolved from HLW sludge using oxygen or air. Our results also show that increasing the hydroxide concetration will increase the rate of reaction and decrease the required operating pressures to near ambient.

Planned Activities

The activities related to this project will continue in two directions: high temperature dissolution using nitrate and lower temperature dissolution using oxygen. The effects of process parameters (temperature, pressure, and concentration) will be continuously evaluated. Different forms of chromium(III) oxides possibly present in HLW waste and the effect of organic and inorganic compounds will be examined.

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

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Research Objective

Our goal is to provide fundamental mechanistic studies of laser produced particulate formation in support of the use of Laser Assisted-Inductively Coupled Plasma-Mass Spectroscopy (LA-ICP-MS) to be used for analysis of radioactive/toxic materials.

Research Progress and Implications

The work reported here represents the first nine months of this 3-year project. The major focus of these studies is determining the detailed mechanisms and character of the particulates generated by laser ablation of solid targets relevant to sampling materials for chemical analysis using inductively coupled mass spectroscopy, ICP-MS. In this application, particles generated by laser ablation must be transported to the plasma "torch" of the ICP-MS, often through a hollow tube with an interior diameter of a few μm. Proper digestion and ionization of particles in the plasma limits particle sizes to under a micron. Thus the production of submicron particles which truly represent the stoichiometry of the specimen is of critical importance.

We have initiated fundamental studies of the mechanisms and resulting characteristics of particulate formation by laser ablation of single crystal materials. One material under study at WSU is a wide bandgap ionic material with relatively low melting point to easily trigger the numerous electronic, thermal, and mechanical processes contributing to particulate formation. This material, $NaNO_3$, has a reasonably high sensitivity to defect formation via exposure to ionizing radiation and by mechanical deformation. This allows us to vary the laser fluence thresholds for a number of these processes.

Pulsed UV laser radiation (248 nm KrF excimer) at high fluences (> 10 J/cm^2, 30 ns pulses) of $NaNO_3$ produces large numbers of particles. Irradiation in air or vacuum produces large spherical particles (> 10 μm in diameter) due to shock-induced spallation of melted surface material. The majority of the particulates are under < 1 μm in diameter and are produced by "hydrodynamic sputtering," where repeated melting and solidification, with the associated thermal expansion and cooling, induce asperity growth and tip ejection over the course of many laser pulses. We have developed a one-dimensional numerical model of the formation and propagation of laser induced shock waves, which verifies that the tensile stresses in the melt layer are sufficient for liquid spallation. In addition, the numerical model provided estimates of the peak surface velocity, which we input into models of hydrodynamic sputtering to predict the minimum particle sizes produced by this means. To date the hydrodynamic sputtering model is consistent with the experimentally observed production of small particles.

Although hydrodynamic sputtering produces large numbers of particles in the size range desired for laser-ablation ICP-MS, there is considerable concern that the repeated melting and solidification required for asperity growth and will alter the stoichiometry of the sampled vs. original material. At PNNL we are using Raman spectroscopy and Secondary Ion Mass Spectroscopy of collected particles to test for this fractionation using $NaNO_3$ grown with 0.01 to 10 % Cs doping. Similar spectroscopy and dissolution ICP-MS of the original samples is being performed on the as-grown material for

comparison.

A promising approach to the production of stoichiometric particles that we are pursuing is optimizing laser-induced fracture. Fracture has negligible effect on the composition of micron and sub-micron-sized particles relative to the original sample. The chief concern is the ability of fracture to produce sufficiently small particles. Initial tests of $NaNO_3$ single crystals with 8 ns 1064-nm laser pulses (Nd:YAG fundamental) show that melting is hindered significantly relative to 248 nm pulses. Hydrodynamic sputtering is avoided by using single laser pulses to generate the fracture. Although sodium nitrate is quite transparent at 1064 nm, sufficient absorption is obtained at fluences below 10 J/cm^2 (7 ns pulses) to produce the required particles. This unconventional particle generation mechanism is associated with a departure from conventional wisdom, where UV lasers have been reported to produce more stoichiometric emission products due to the relatively high absorption of most materials at UV wavelengths. Target surface morphology and ejected particulate characterization are showing that over a range of fluences, fracture is indeed producing particles of the desired size for ICP-MS.

Studies at PNNL as part of this program have focused on the use of optical particle size measurements in conjunction with LA/ICP-MS to determine the laser pulse energies, pulse lengths and focal areas that produce particle size distributions that maximize performance of LA/ICP-MS. The samples studied have included simulants of vitrified waste and tank waste simulants as well as more idealized samples such as calcium carbonate, copper and aluminum. These samples span a large range of optical and physical properties relevant to the laser ablation process, representative of the properties. This is similar to the range of properties expected in Pu wasteforms including tank waste, contaminated equipment as well as pure Pu metal and oxide samples. Analytical performance was measured in terms of sensitivity, precision, and accuracy. The focal offset (distance from the laser focus to the surface) was varied to cover a wide range of fluence and pulse energies.

The first studies were performed using a 10 ns ablation pulse length at 355 nm. Pulse energies from 50 uJ/pulse to 3 mJ were used, corresponding to energy densities of < .1 J/cm^2 to 20 J/cm^2 over the range of focal offsets employed. The relative degree of laser-induced plasma and particulate formation was tested by comparing the relative population of particulates, ions and neutral species as a function of focal offset. These quantities were measured by a combination of light scattering and optical absorption spectroscopy with a CW dye laser. Results were markedly different for samples with low thermal conductivity (glasses, simulants, chalk) than for the metal samples. Particulate production from laser ablation of the poor thermal conductors exhibits maxima on either side of the focal point. This corresponds to energy densities below or at the threshold for generation of a laser-induced plasma. The metal samples showed a much weaker dependence on the focal offset, with a slight maximum at the focal point. The maximum in the particle size distribution from ablation of the poor conductors is from .2, 1 micron while ablation of the metals primarily produces particles < .2 microns.

Picosecond (15-20 ps) ablation studies of the poor thermal conductors showed that the dependence of the particulate production on focal offset depends on the total pulse energy, or the number of photons striking the surface, rather than the fluence. These results suggest that the production of particulates is not strongly coupled to the formation of a laser-induced plasma. When the metal samples were ablated with picosecond pulses, the focal offset behavior displayed slight maxima away from the focal point, suggesting that thermal conductivity may constrain/define the laser parameters for optimum production of particulates suitable for analysis by ICP-MS. Also being studied with WSU is what role fracture vs. melting is playing in the particulate production for low thermal conductivity materials.

Planned Activities

In the next 15 months we plan to continue the Nd:YAG induced fracture studies on “transparent” materials in both air and vacuum to better understand the particle size determining mechanisms and to work jointly on measurement and minimization of fractionation. We also will examine more closely the trajectories of the various types of particles to determine possible separation schemes to improve selection of the “best” particles. Electric charge on the fracture induced ejecta has been

demonstrated and will be examined as a possible means of separation. Further studies using shorter (fs) pulses will be investigated to determine what role pulse width has on tye types of particles produced. Finally, additional modeling and simulations of the thermal-mechanical processes will be carried out to clarify mechanisms. These efforts will be coordinated and performed on the same materials to maximize their impact on chemical analysis technology.

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

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Research Objective

This EMSP research endeavors to understand fundamental laser-ablation sampling processes and to determine the influence of these processes on analytical characterization of EM waste-site samples. The issues germane to the EMSP are sensitivity and accuracy of analysis. These issues are researched by studying fractionation, sample transport, mass loading, and analytical system optimization. Inductively coupled plasma - mass spectroscopy (ICP-MS) is emphasized in this research because of its use throughout the DOE labs and sites.

Research Progress and Implications

This report summarizes research performed over the first half of this three-year program. Four issues were emphasized to improve analytical sensitivity and accuracy, including the time dependent laser removal of mass from a solid sample, fractionation, particle generation and transport, and optimization of the ICP-MS for laser ablation sampling. This research has led to six journal publications.

One of the first issues addressed was that of accuracy of chemical characterization from mixed-component samples. We identified two primary parameters that effect accuracy, mass loading in the ICP and fractionation (preferential removal of elements based on vapor pressure) (1). When the laser beam ablates the sample, a significant portion of mass is transported to the ICP. If the temperature or electron number density in the ICP is perturbed by this mass, accuracy will be compromised. We investigated mass loading by ablating samples using a wide range of laser properties (2). The temperature of the ICP was measured using a ratio of Fe emission lines, and the electron number density was measured using a ratio of Mg ion to emission lines. Using a nanosecond-pulsed Nd:YAG laser, which is similar to those used in the commercial laser ablation attachments, we identified laser power densities in which mass loading was not significant for a number of samples. However, there were samples in which these same power densities did cause mass loading, such as glasses and soils. Further studies of ICP and laser conditions need to be completed for these samples.

Fractionation (mass removal based on thermal properties) continues to be one of the most difficult problems effecting accuracy of laser ablation sampling. In this research, we investigated the effect of fractionation for two different cases, fractionation as a function of elemental composition in a suite of alloys (3) and as a function of time (4). The number of laser pulses at a fixed location on the sample and the laser power density were found to have a significant influence on fractionation. We found that it is almost impossible to completely eliminate fractionation from many samples, including alloys, ceramics, glasses, and other refractory materials. The extent of fractionation depends on the concentration of the volatile elements; the lower the concentration, the greater the degree of

fractionation (3). Even though fractionation exists, it is possible to use solid standards to calibrate the ICP, assuming that fractionation from the standards is similar to that in the sample. ICP-MS data for a suite of elements versus concentration showed a linear relationship with good correlation by using NIST and three other glass samples. However, standards are not likely to be available for waste-site samples; studies will continue in order to better understand and eliminate fractionation for these samples.

Analytical sensitivity was addressed by studying ways to enhance the laser ablation efficiency and by optimizing the ICP-MS system for dry sample introduction. Optimization of sample-gas flow rate, ICP power, and ICP-MS lens voltages was performed. We demonstrated that the sensitivity could be enhanced by over an order of magnitude by optimizing these parameters, for the dry sample vapor characteristic of laser ablation. The reduction of space charge in the MS is thought to be responsible for the increased sensitivity when the ICP was optimized. The use of different noble gases in the ablation chamber also was found to enhance sensitivity. The enhancement was found to be dependent on the laser's pulse duration. For the nanosecond-pulsed laser, helium and neon provided an increased mass ablation efficiency. For picosecond laser ablation sampling, only helium provided an enhancement (5,6). We demonstrated enhanced sensitivity by almost three orders of magnitude by using picosecond UV compared to nanosecond IR laser ablation, and helium gas. The enhanced sensitivity is beneficial for detecting trace contaminants in EM waste-site samples.

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Planned Activities

The general thrust of understanding laser ablation sampling and improving analytical capabilities will continue. Immediate plans are to write a seventh manuscript describing the optimization of the ICP-MS system for laser ablation sampling. We will continue to study the effects of fractionation. A primary quest will be to determine where fractionation occurs; is it occurring at the ablation site during the laser pulse, during the plasma-sample interaction, during particle nucleation and/or particle transport, or in the ICP itself. Another area that will be investigated is particle generation and transport, and sample chamber design. For liquid samples, extensive studies have been carried out on the design of nebulization chambers for accurate and sensitive chemical analysis. Laser ablation sample chambers and dry-vapor transport studies are preliminary, and not conclusive in defining general parameters for chemical analysis. Entrainment of ablated mass into the gas and transport to the ICP is particle size dependent. Transport efficiency needs to be accurately determined as a function of particle-size distribution. The size and composition of the particles may also effect fractionation. Also, we plan to perform the laser ablation sampling studies using samples that are germane to the EMSP mission. Carol Jansen at the Savannah River Site is in the process of sending prototypic waste-glass samples.

Development of Inorganic Ion Exchangers for Nuclear Waste Remediation

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Research Objective

To expand our efforts to provide families of inorganic ion exchangers useful on a global scale. In carrying out this objective, we will synthesize a variety of ion exchange materials, determine their structures and where necessary alter these structures to build in the desired properties. The underlying thermodynamic, kinetic and molecular basis of ion exchange behavior will be elucidated and their suitability for nuclear waste remediation will be assessed.

Research Progress and Implications

As of September 1, 1996, we have synthesized a number of highly selective inorganic ion exchangers, determined their crystal structures and elucidated the mechanism of exchange for a number of these exchangers.

1. $Na_2Ti_2O_3SiO_4 \sum 2H_2O$ (CST). This compound is the most highly selective Cs^+ exchanger known and is also selective for Sr^{2+}. The structure of this compound was solved from powder data[1] and found to have a framework structure enclosing unidimensional tunnels. For alkali metals the exchange sites were found to vary depending upon the size of the cation. Li^+ and Na^+ are small enough to fit into framework sites which accommodate half the required cations. The remainder lie within the tunnels. The larger Cs^+ cannot fit into the framework sites and can occupy only half the tunnel sites. Thus, only 25% of the total exchanger sites is available to Cs^+. However, the Cs^+-O bonds that form are exactly equal to the sum of the radii for Cs^+ and O^{2-}. All other cations have a poorer fit and tend to be displaced for Cs^+. In the presence of Na^+ dual exchange occurs simultaneously[3] as Na^+ fills the framework sites and a second site inside the tunnels. As the sodium ion concentration increases the uptake of Cs^+ decreases and is only 0.05-0.1 meq/g in simulants of Hanford Tank Waste Solutions.

We have recently carried out a neutron diffraction study of $H_2Ti_2O_3SiO_4$. All the protons reside on the oxygens bonded to titanium. Addition of water results in about half the protons forming hydronium ion within the tunnels.[2] This highly acid character of the protons we attribute to the fact that the OH oxygens are each bonded to three Ti^{4+} ions. This results in a very high repulsion towards the protons resulting in a high ionization constant. Addition of Cs^+ to this protonated form at pH2 results in saturation of the Cs^+ site to form $Cs_{0.5}H_{1.5}Ti_2O_3SiO_4 \bullet 2H_2O$.

Planned Activities

Implications and Planned Activities. We now understand how this (misnamed) crystalline silicotitante (CST) is able to take up Cs^+ from highly acid and basic solutions containing high levels of electrolyte. We are obtaining thermodynamic data and obtain kinetic data. This combination of

structural, thermodynamic and kinetic data will allow engineers to apply this exchange to a variety of remediation problems. Structural studies relevant to Sr^{2+} exchange are planned for the near future. Substitutions within the framework will also be carried out.

2. Trisilicates: $M(I)_2M(IV)\ Si_3O_9 \sum H_2O$, (M(I) = Na^+, K^+ , M(IV) = Ti, Sn Zr, Ce). We have prepared a family of trisilicates and solved the crystal structures of three of them.[4, 5] These compounds have framework structures enclosing alternating large and small cavities. The cavity sizes vary with the size of the M(IV) cation. For example, the Ti phase does not take up Cs^+ but the Zr phase exhibits very high Kd values for Cs^+ (10^5 ml/g in groundwaters) and is even 1500 ml/g in 6M NaOH. The mixed phase $Na_2Zr_{0.75}Sn_{0.25}(Si_3O_9)\sum H_2O$ shows even higher Kd values. The interchangeability of the M(IV) ion changes the size of the cavities and governs the selectivity. This is an excellent example of crystal engineering. The mechanism of exchange is complex involving both cavities.

Implications and Planned Activities This family of exchangers can be prepared hydrothermally and should not be too expensive ($5 - $10 per lbs.). It can be utilized for groundwater remediation and process waters which are alkaline. We plan to analyze the wealth of structural data we have accumulated in the light of the ion exchange behavior and to examine their behavior towards divalent metals. We have already shown that we can remove Pb^{2+} and Cd^{2+} from contaminated effluents. Further structural work will be carried out to elucidate the exchange mechanism (siting of ions) prior to thermodynamic and kinetic studies.

3. Pharmacosiderites: We have prepared a family of compounds based on the pharmacosiderite mineral structure[6] solved their structures and determined the ion siting. The titanium silicate version, $K_3H(TiO)_4(SiO_4)_3 \sum nH_2O$ has a structure that is similar to that of the CST compound. It exhibits a high affinity for both Cs^+ and Sr^{2+}.[7] The Kd values have been considerably improved by partial substitution of Ge for Ti.[8] The strucutre of the Sr^{2+} phase is under investigation.

Implications and Planned Activities This study is another example of crystal engineering and we will continue to make additional substitutions by a computer modeling procedure to arrive at the best structure for exchange of Cs^+ and for Sr^{2+}. We will also probe the acidity of the proton form to compare with the CST. We have made a start on developing a theory of ion exchange behavior in tight tunnel structures and will use it as a guide in understanding the effect of different electrolytes on the selectivity in this and other similar exchangers.

Summary of Additional Studies

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

Implications and Planned Activities Nuclear waste systems are highly diverse and one remediation process will surely not suffice for this diversity. Hence our global approach. In process and testing are four more few families of exchangers.

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

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Research Objective

The purpose of this task is to undertake the design, synthesis, and characterization of the next generation of crown ethers for metal-ion separations applicable to USDOE's environmental needs. Target problems include: Li^+ ions leaching from burial sites at the Oak Ridge Y-12 Plant; fission products ^{90}Sr and ^{137}Cs contaminating high-level tank wastes at Hanford, INEEL, and Savannah River; and radium in wastes at the Niagara Falls Storage Site. Unfortunately, the technologies needed to address these problems either do not exist or exhibit substantial deficiencies. Separation techniques such as solvent extraction and ion exchange promise to play a strong role, especially as enhanced with highly selective crown ethers and calixarenes.

Research Progress and Implications

This project is midway through year 2 of a 3-year effort. Below is given a summary of progress in the approximate period September, 1997, to May, 1998, for each of the four co-investigators at Pacific Northwest National Laboratory (PNNL), Argonne National Laboratory (ANL), Oak Ridge National Laboratory (ORNL), and the University of Tennessee (UTK). The overall approach entails utilization of theory and molecular modeling (PNNL), organic synthesis of novel crown compounds (ORNL), solvent extraction studies (ORNL and ANL), and studies of polymer-immobilized crown ethers (UTK).

Molecular Modeling (J. B. Nicholas, D. A. Dixon, and B. P. Hay, PNNL). Towards increasing the selectivity of calixarene-crown sequestering agents for cesium, effort in FY98 has concerned the role that the pi-cation interactions play in the complexation of alkali metal ions by calixarenes. The various modes of cation binding to a calixarene conformation differ with respect to the number of oxygens and arenes that serve as donor groups. To better understand the energetics and geometries of these interactions, we have completed high-level MP2/dzvp+ calculations on complexes of the alkali cations with benzene and anisole. Non-local density functional theory calculations are being used to identify all stable binding modes of tetramethoxy-calix[4]arene with sodium and cesium and to rank these modes in order of stability. Calculations at the B3LYP/dzvp level have been in progress on the EMSL supercomputer since the start of the fiscal year. So far we have determined

the relative energies of the cone, partial cone, 1,3 alternate, and 1,2 alternate forms of tetramethoxy-calix[4]arene and have located eight minima for binding sodium by these conformers.

Univalent Metal Ions (R. A. Sachleben, J. C. Bryan, T. J. Haverlock, and B. A. Moyer, ORNL). A notable accomplishment in the past year was the development of improved syntheses of calix[4]arene-biscrown ethers and bis-alkyloxy calix[4]arene-crown ethers. Resulting lower costs for these important extractants directly benefit the development of processes for Cs removal from tank waste under funding by the Efficient Separations and Processing (ESP) Crosscutting Program. In addition, detailed solvent-extraction studies aided by computer equilibrium modeling have revealed the underlying extraction equilibria by which Cs^+ ion is extracted by calix[4]arene-bis(t-octylbenzo-crown-6) in a model diluent, 1,2-dichloroethane. It has also been shown that the Cs/K separation factor for this extractant depends upon several environmental factors. These insights have been useful in interpreting and improving extraction and stripping behavior in process flowsheet development under ESP.

Guided by molecular-modeling results at PNNL, a series of 15 novel calix[4]arene-crown compounds has been synthesized in the past year toward understanding effects of substituents on the calixarene ring and on the attached crown-6 bridge. We have shown that systematic changes in the bulkiness of particular substituent groups effect changes both in the conformations observed in crystal structures, extraction strength, and Cs/K selectivity. This result has led to a new class of calix[4]arene-crown ethers with Cs/K selectivity an order of magnitude greater than the previously reported calix[4]arene-crown-6 compounds.

Divalent Metal Ions (M. L. Dietz and R. Chiarizia, ANL). In an effort to develop guidelines for the rational design of synergistic extraction systems for alkaline earth cation separations employing crown ethers, we have been examining combinations of dialkylphosphoric acids with pure isomers of dicyclohexano-18-crown-6 ($DCH_{18}C_6$). The extent of interaction between each of the organophosphorus extractants and the various crown ether stereoisomers has been investigated in detail using solvent extraction, infrared spectroscopy, and vapor phase osmometry. The osmometric studies indicate that each of the dialkylphosphoric acids exists as a dimer in toluene, while the $DCH_{18}C_6$ stereoisomers are monomeric. In addition, the VPO results indicate no interaction between $DCH_{18}C_6$ and the organophosphorus acids. Extraction data indicate that the extracted species in each of the systems is of the form $M(DCH_{18}C_6)(HA_2)^2$ (where M = Sr^{2+} or Ba^{2+}). Continuous variation studies employing dialkylphosphoric acid / $DCH_{18}C_6$ mixtures show only small synergistic effects in the extraction of calcium ion. For barium and strontium, however, appreciable synergistic effects are observed upon addition of the cis-syn-cis (A) isomer, while other isomers show less effect. In all cases in which synergism is observed, the ratio of dialkylphosphoric acid to $DCH_{18}C_6$ in the extracted complex has been found to be 4:1 (2 acid dimers to 1 crown ether molecule). The pH, dialkylphosphoric acid, and $DCH_{18}C_6$ dependencies in the synergistic systems exhibit slopes near 2, 2, and 1, respectively.

Polymer-Immobilized Crown Ethers (S.D. Alexandratos, UTK; R.A. Sachleben, T.J. Haverlock, and B.A. Moyer, ORNL). The synthesis effort at the University of Tennessee has focused on immobilizing the crown ether monomers received from ORNL. Early experiments established that the crown with the methylene group off of the ring was incapable of polymerizing directly into a macromolecular structure. It was then decided to attempt the immobilization of the crown compound onto a polymer support already containing a group capable of covalently bonding the crown. Five different approaches were devised, and experiments are continuing within each approach. Results have been obtained on the following two of the approaches: (1) Schiff base formation of polystyrene-containing-CH_2NH_2 groups with keto-crown. (2) Immobilization of the methylene-containing crown with polystyrene containing a relatively acidic C-H bond was attempted with polystyrene containing the beta-ketophosphonate ligand. Unfortunately, extraction tests of the corresponding two resin samples provided to ORNL have revealed that the first does not extract alkali metals detectably and that the second is relatively nonselective.

Planned Activities

At PNNL, calculations are currently in progress for binding of cesium ion by tetramethoxy-calix[4]arene. The results will be used to understand Cs/Na selectivity. Efforts at ANL to model the

extraction equilibria for the synergistic systems, to examine possible correlations between ligand strain energy and synergistic effects, and to extend this work to solid-supported systems are now in progress. At ORNL, efforts will be made to attach ionizable groups to calix[4]arene-crown-6 compounds. Polymer synthesis at UTK will focus on three alternative means for attaching 14-crown-4 ethers to suitable immobilized functional groups.

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Polyoxometalates for Radioactive Waste Treatment

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Research Objective

This research is directed towards the use of polyoxoanions of the early transition metals (primarily tungsten) as possible sequestrants and storage matrices for lanthanide, actinide, and technetium species. The latter substances are important radioactive components of tank wastes from spent commercial nuclear fuel, but are present in low proportion by mass. Technetium is a particularly troublesome component because it is highly mobile in groundwater and is volatilized in vitrification processes currently under examination for long-term storage. Scientific goals: synthesis and characterization of new and selective polyoxotungstate complexes of Ln^{3+}, An^{4+}, UO_2^{2+}; exploration of stable polyoxoanions containing Tc (using, in the first instance, Re as a nonradioactive surrogate); thermal conversion of polytungstate complexes to tungsten bronze materials for their evaluation as inert storage matrices.

Research Progress and Implications

This report summarizes the results after 20 months of a 3-year project.

1. *Selective sequestration of Ln^{3+} and U^{4+} by $[NaP_5W_{30}O_{110}]^{14-}$ (I).* Replacement of the central sodium cation in **I** (a doughnut-shaped anion with approximate D_{5h} symmetry) by Ln^{3+} and U^{4+}under hydrothermal conditions has been conditions has been shown to be highly selective for the multivalent cations in neutral or weakly acidic solutions. For example, Nd^{3+} is incorporated with ~60% yield in the presence of a 200-fold molar excess of Na^+, which is a major component of tank wastes. Other major components, such as Fe^{3+} and Al^{3+} are not complexed by **I** and do not interfere with lanthanide incorporation. Structural studies of the complexes with central Na^+, Ca^{2+}, Eu^{3+}, and U^{4+} reveal an axially-coordinated water molecule, the protons of which undergo very slow exchange with solvent water in neutral solution. All three isotopomers (with coordinated HOH, HOD, and DOD) are distinguishable by P-nmr of the paramagnetic complexes.
2. *Diastereomers of 1:2 complexes of An^{4+} with ÿ l -$[P_2W_{17}O_{61}]^{10-}$(II).* Anion **II** has a structure of C_1 symmetry and in principle should yield chiral syn and anti isomers of $[An(P_2W_{17}O_{61})_2]^{16-}$, based on a nominal square antiprism coordination polyhedron for An^{4+}. P-nmr spectra of the U^{4+} and Th^{4+}complexes display multiple sets of resonances consistent with the presence of several diastereomers. Single crystal X-ray investigation of U and Th complexes show an anti conformation for the former and a syn conformation for the latter.
3. *New giant heteropolytungstate complexes of Ln^{3+}.* Several new complexes incorporating the tungstoarsenate(III) building block, $[AsW^9O^{33}]^{9-}$ (**III**), are formed in good yields in neutral aqueous solution from appropriate mixtures of the Ln^{3+}, AsO_2ÿ, and WO_4^{2-}. In addition to structurally-characterized As ^{3}Ce2W_{29} and $As_5Ce_4W^{39}$ polyoxoanions, the new species include the largest known discrete polytungstate anions, $[As_{12}Ln_{16}(H_2O)_{36}W_{184}O_{524}]^{76-}$,(**IV**); Ln = La, Ce, Nd, Sm. The structure of **IV** is disk-shaped with a diameter of 4 nm, and the anion has a molar mass of ca 40,000. According to W-NMR the anion structure is stable in aqueous solution, and the ammonium salts of these anions are recrystallizable in the presence of Na+. Among other large complexes are species with $[As_4W_{40}O_{140}]^{28-}$ building blocks.
4. *Heteropolytungstates containing UO_2^{2+}.* The first examples of polytungstate complexes which incorporate the uranyl cation have been prepared and characterized. In every case the uranium atom adopts a pentagonal bipyramidal coordination geometry. Complexes incorporating anion **III** as building blocks include [(UO2)3(H2O)6As3W30O105]15- with C3v symmetry. Other species include novel cation-dependent structures based on the two building blocks

[PW9O34]9- or [SiW9O34]10-, and a W40 structure based on four ÿ-[SiW10O36]8- units. All new complexes are formed in good yield from neutral or weakly acidic solutions.

5. *Thermal conversions of complexes*. Based upon TGA data, the ammonium-sodium [(NH4)70Na6] salt of **IV** was heated in hydrogen atmosphere to 550?C followed by a 3-h isothermal treatment in argon at 920°. The product was the cubic bronze Na0.04Ce0.108WO3 according to X-ray powder diffraction and elemental analysis. Formation of the cerium tungsten bronze has therefore occurred at a much lower temperature than has been previously reported. At somewhat lower temperatures, the hexagonal bronzes are generated
6. *Polyoxoanion complexes of Re (Tc).* Most attention has been focused on the tetravalent (d3) oxidation state of Re since this is known to yield inert octahedral complexes. Several heteropolyanions incorporating isoelectronic Mn4+ are well characterized, and the initial target species were the Anderson anions [ReM6O24]8- (M = Mo,W). It has proved difficult to identify these species, and we have recently moved to evaluate possible niobate complexes (analogues of [M(Nb6O19)2]12-, M = tetravalent Mn and Ni). Very recently we have obtained encouraging results from this approach.

Planned Activities

The synthesis/characterization phase of the lanthanide and actinide complexes (sections 1 - 4 above) is now virtually complete, and has been published or is in preparation for publication. Attention is now directed towards sub-projects 5 and 6 above.

TGA examination of the several tungstolanthanates described in section 3 indicates that they, like **IV**, should be convertible to bronzes at relatively low temperatures. The uranyl derivatives (section 4) will also be subjected to TGA and reductive thermal degradation to bronzes will be developed. Long term hydrolytic/oxidative stability of the bronzes will be explored.

Characterization of the recently discovered nioborhenate complexes (section 6) will assume high priority. These species are particularly attractive since they are stable in alkaline solutions - conditions which prevail in the Hanford tank wastes. Parallel synthetic and characterization procedures involving Tc are to be carried out in collaboration with Dr. Jeffrey Bryan at Oak Ridge National Laboratory.

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Potential-Modulated Intercalation of Alkali Cations into Metal Hexacyanoferrate Coated Electrodes

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Research Objective

This program is studying potential-driven cation intercalation and deintercalation in metal hexacyanoferrate compounds, with the eventual goal of creating materials with high selectivity for cesium separations and long cycle lifetimes. The separation of radiocesium from other benign cations has important implications for the cost of processing a variety of cesium contaminated DOE wasteforms.

Research Progress and Implications

This report summarizes results after nine months of work. Much of the initial efforts have been directed towards quantitatively characterizing the selectivity of nickel hexacyanoferrate derivatized electrodes for intercalating cesium preferentially over other alkali metal cations. Using energy dispersive xray spectroscopy (ex-situ, but non-destructive) and ICP analysis (ex-situ and destructive), we have demonstrated that the nickel hexacyanoferrate lattice has a strong preference for intercalated cesium over sodium. For example, when ions are reversibly loaded into a nickel hexacyanoferrate thin film from a solution containing 0.9999 M Na^+ and 0.0001 M Cs^+, the film intercalates 40% as much Cs^+ as when loaded from pure 1 M Cs^+ containing electrolyte (all electrolytes use nitrates as the common anion). We have also shown that, contrary to the common assumptions found in the literature, a significant fraction of the thin film is not active initially. A new near infrared laser has been purchased and is being added to our Raman spectroscopy facilities to allow in-situ studies of the intercalation processes.

Planned Activities

We are just beginning to look at other metal hexacyanoferrate compounds, the use of chemometric methods to quantify the Cs content of the thin films more readily using electrochemical methods alone, and also to use quartz crystal microbalance studies to measure selectivity in the form of weight gain. Raman spectroscopy at longer wavelengths than currently achieveable will also come on line soon. These studies should become routine in our laboratory in the next 6-8 months. These new in-situ characterization techniques are expected to lead to a better understanding of the the processing-structure-property relationships that control the ion intercalation behavior in these materials.

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

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Debra T. Bostick, Oak Ridge National Laboratory
Peter W. Carr, University of Minnesota

Research Objective

The overall objective of this research is to develop and enhance our understanding of the chemical equilibria for major organic complexant species and their products with metals in an aqueous mixture such as the mixtures of DOE stored wastes. Our approach to achieving this objective is a series of incremental studies involving cooperative efforts at Oak Ridge National Laboratory and at the University of Minnesota. Investigations at ORNL are characterizing soft ionization mass spectrometry processes for the complexant species by developing and interpreting positive and negative ion thermospray mass spectrometry of some organic complexants and their decomposition products and relating the spectral distributions to gas phase chemistry. Subsequently this knowledge of the gas phase chemistry will be related to known solution chemistry behavior. At the University of Minnesota liquid chromatography separations on zirconia-based chromatographic supports (including bare zirconia dynamically modified with Lewis bases and PEI-coated zirconia) are being studied in order to understand the separation of organic complexants and the products formed by complexants with metals in complex aqueous mixtures; and thereby define the conditions needed to introduce a simplified chemical stream into the mass spectrometer. Ultimately, the knowledge gained from these parallel efforts will be combined at Oak Ridge National Laboratory to characterize the complexant species in a multi-component aqueous mixture with the final objective being to develop data needed to define chemical equilibria for complexant species in such multi-component mixtures.

Research Progress and Implications

This is a three-year project which started on October 1, 1997. This report summarizes the progress achieved for the first eight months of the study (through May, 1998). Thermospray positive ion mass spectra of seven different organic complexants have been defined in a water:methanol (1:1 by volume) solvent system that was buffered with 0.1 M ammonium acetate (pH = 6.7). These complexants were imidodiacetic acid (IDA), ethylenediamine-N,N'-diacetic acid (EDDA), N-(2-hydroxyethyl)iminodiacetic acid (HEIDA), nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Mass spectra of all these complexants showed a peak at mass $[M+1]^+$ when vaporized from this solvent medium. Only NTA showed a significant peak at mass $[M+18]^+$ which was interpreted as the formation of an adduct with an ammonium ion from the buffered solvent medium. This observation for the vaporized NTA is consistent with the measured acidity in aqueous solution where the first acid dissociation for NTA has a lower pK value than those reported for EDTA, HEDTA, and IDA (1). This tendency to form an ammonium adduct in the gas phase would indicate that NTA has a lower proton affinity than the other complexants in the vaporized phase. This lower proton affinity in the vapor phase would be consistent with the greater observed acidity in the solution phase. Accordingly, this observation provides an indication that characteristics observed after thermospray vaporization may aid in defining behavior in solution. Such interpretations of thermospray mass spectra should be useful in the characterization of DOE mixed waste solutions.

Progress has also been made in developing thermospray mass spectra at source temperatures of less than 170° C. Such lower source temperatures should reduce the amount to thermal degradation for labile species. Pressures in the analyzer chamber of the mass spectrometer tend to elevate as the thermospray source temperature is reduced; however, the instrument has been operated for up to 8 hours at a source temperature of 175° C and a solvent flow of 1 ml/min. This time interval is of sufficient duration to analyze multiple liquid chromatography separations.

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Planned Activities

The subcontract to provide for the collaborative studies at the University of Minnesota has only recently been established (May 1998). Thus activity at both ORNL and the University of Minnesota will greatly intensify during the next four months with the planned schedule as follows:

—07/98: Complete evaluation of relative proton affinities and gas phase acidities of organic complexants after thermospray vaporization
—12/98: Complete separation studies on bare zirconia dynamically modified with Lewis bases.
—03/99: Evaluate predictive capability of proton affinity/gas phase acidity/TSMS characteristics
—09/99: Complete study of chromatographic properties of PEI-coated zirconia.
—11/99: Complete TSMS studies of some known chemical species of complexants and metal ions.
—09/00: Complete manuscripts for open literature describing results of these studies.

Other Access To Information

Results from these investigations will be published in the open literature. At this point in time only minimal resources have been expended and no publications have been generated.

High Temperature Condensed Phase Mass Spectrometric Analysis

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

Research Objective

The purposes of this program are to design and construct a mass spectrometer for the analysis of high temperature condensed phase materials, and to use this instrument to investigate the high temperature chemistry of waste form materials. Individual mass spectrometric techniques can provide windows through which to view selected properties of materials at high temperatures, but information from several sources must be combined to obtain the larger picture. This instrument is designed to provide several types of interlaced mass spectrometric analyses from a single specimen, eliminating the uncertainties associated with combining data from several different samples analyzed in different instruments.

Research Progress and Implications

The features that are being combined in this instrument are:

1. Miniaturized sample mounting and control of sample temperature to 1300C.
2. Electron impact (EI) ionization of volatilized neutrals.
3. Surface ionization, positive and negative ions.
4. Secondary ion mass spectrometry (SIMS), positive and negative ions.
5. Ultrahigh vacuum combined with sputtering to allow surface analyses to be related to bulk composition.
6. A single mass analyzer able to sequentially analyze ions from each of the ionization modes.

These features will allow the following types of information to be obtained:

1. Atomic and molecular species vaporizing from the surface, both neutral and ionic. Neutrals will predominate in almost all systems, but the positive and negative ions which do volatize give valuable insights into the condensed phase chemistry.
2. SIMS interrogation of the surface composition, with ions sputtered from the surface analyzed by mass spectrometry. A high intensity sputter ion gun will be used to clean the surface, while a lower intensity ion gun will be used for the SIMS analysis. The ultrahigh vacuum will allow the surface to be maintained in a clean configuration until the analysis can be completed. This in turn gives information concerning the bulk composition of the material.
3. This information is obtained as a function of temperature from a single sample, so the interpretation of events will be more straight forward than merging data from different instruments.

There currently are two instruments operating in our laboratory that perform these functions; one for SIMS and surface ionization on high temperature samples, and the other for EI and surface ionization. These have provided valuable insights into the properties of materials at high temperatures, but there is uncertainty from the perspective that all analyses cannot be performed on the same sample and from the fact that neither can guarantee a clean surface.

Planned Activities

The types of research which can be conducted with this instrument are many and varied. One example which was used in the original proposal is the concept of developing ceramic and glass materials with charge centers (sometimes called color centers or F-centers) deliberately induced to greatly reduce the migration of ionic species through the material at high temperatures. This concept originates from studies conducted on a BES Chem Sciences program in which it was shown that these charge centers, if allowed to accumulate, shut down ion migration and emission in high temperature ion emitters. Waste forms developed from this concept would have built-in mechanisms to prevent the migration of ionic species. The mass spectrometer system under development will be ideal for researching this concept.

A second example is the issue of acidic/basic conditions within the condensed state and how this relates to ion migration for different species. Rhenium is a near perfect stand-in for technetium, an important fission product requiring million year storage. Studies with rhenium indicate that keeping the condensed state acidic reduces the volatility of rhenium by forcing the +7 rhenium oxide (volatile and non-ionic) to perrhenate (also +7, but ionic and much less volatile), the migration of which can be shut down by inducing charge centers. Again, the instrument is well suited for this type of study, since it can measure volatilizing species while at the same time identifying the responsible condensed state species.

The preliminary instrument design has been completed, and many of the components ordered. The largest design effort has gone into the main chamber to ensure the compatibility of the various ionization modes with each other and with ultra high vacuum conditions. This chamber is expected to be delivered in June. The vacuum system is designed to be baked, with the main pumping coming from a 500l/sec. triode ion pump, a liquid nitrogen cryoshroud, and a titanium sublimator. The vacuum lock and the ion guns will be differentially pumped with a turbo pump. The system should easily

pump into the 10's when the sample stage is cold, and should hold in the low 9's when a sample is at maximum temperature (1300° C). This will allow the surface of the hot samples to be maintained in a "clean" state so as to allow the SIMS analysis of the surface to be representative of the bulk following cleaning by sputtering.

Preliminary designs of the ion optics have been developed which look quite promising. An iterative approach is being taken in the implementation of the combined ion source. The SIMS component will be the most difficult to implement, hence the main design effort has gone into this aspect of the instrument. Surface ions are readily obtained from an implementation of SIMS, hence pose no problems. The addition of EI to the system without impacting the SIMS capability then becomes the next challenge; some alternate techniques for implementing this feature have been modeled with the ion optics program "SIMION." We have a preferred design and are examining the practicality of implementing the design into a working instrument.

The miniaturized high temperature cell has recently undergone significant improvements, with greatly improved mechanical stability as a function of temperature. The next major design effort will go into adapting this re-designed high temperature cell as the target for the instrument, so that SIMS can be conducted on the surface of the material in the cell, and so that EI can be conducted on the species volatilizing from the surface.

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

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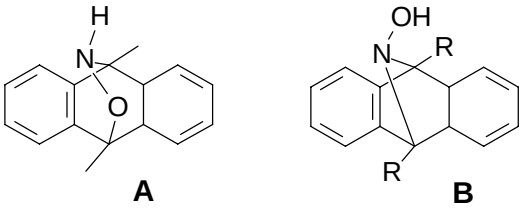
Charles L. Liotta, Georgia Institute of Technology
Henry M. Neumann, Georgia Institute of Technology

Research Objective

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

Research Progress and Implications

During the first 20 mon of this 36 mon project the primary focus has been toward *(1)* the development of precursors that would allow NO^- to be generated rapidly and under controlled conditions, *(2)* further development of models for aluminum catalyzed nitrite oxidation of HEDTA, and *(3)* an analysis of the relative contributions of thermal vs radiolytic pathways for complexant decomposition in tank 101-SY.



A **B**

(1) Precursors to NO^- (S. Seymore, A. Belcher, graduate students; V. Kumar, post-doctoral). The NO^- anion, like isoelectronic O_2, can exist in either the singlet state or the triplet state. Contrary to the considerable experimental and theoretical work on NO^- and its conjugate acids in the gas phase, relatively little is known about the anion in condensed phases although one theoretical study indicates that the triplet state is also the ground state of $(NO{\cdot}2H_2O)_{(g)}$ [3]. Our objective is to discover methods to rapidly generate NO^- in condensed phase under controlled conditions. To this end we have examined the thermal and photochemical reactions of **A**, neither of which occur sufficiently rapidly for our purposes. Studies on the anion of **A** are in progress.

Synthesis of **A** requires 9,10-dimethylanthracene, which although commercially available, is very expensive. A low-cost, facile route to this compound and analogs based upon a nickel catalyzed reaction between 9,10-dibromoanthracene and the appropriate Grignard reagent has been developed. These and other 9,10-dialkylated anthracenes are frequently used in photochemical and photophysics; the synthetic methodology will make these materials more accessible to a broad range of scientists.

Good progress toward the synthesis of precursor **B** has been made, but the unexpected resignation of V. Kumar (post-doctoral) has temporarily halted this phase of the work. This work will resume as soon as a new postdoctoral or graduate student is identified for the project.

Thermal decomposition of Piloty's acid, $PhSO_2NHOH$, under basic conditions has long been believed to generate NO^-.[4] We have reexamined the kinetics of decomposition of this compound and the p-CF_3 derivative. These results suggest a more detailed mechanism for the decomposition of the mono anion than previously proposed (1)-(4).[5] Our results indicate that equilibrium amounts of the dianion, $PhSO_2NO^{2-}$, is formed at high pH ($K_a \sim 10^{-14}$) and that it is unreactive compared to the monoanion. The monoanion of Piloty's acid was earlier suggested to be O-deprotonated based upon Overhauser enhancements in the nitrogen NMR spectrum. [5]

$$PhSO_2NHO^- \rightleftharpoons PhSO_2NOH^- \quad (1)$$

$$PhSO_2NHO^- \longrightarrow PhSO_2^- + HNO \quad (2)$$

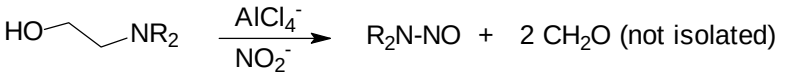
$$PhSO_2NOH^- \rightleftharpoons PhSO_2^- + NOH \quad (3)$$

$$NOH/NHO + OH^- \longrightarrow NO^- + H_2O \quad (4)$$

Although the presence of a second tautomeric form is not excluded by this interpretation we have attempted to acquire chemical evidence for the structure of the anion by alkylation experiments under basic conditions. After several unsuccessful attempts we now have preliminary evidence to

suggest that alkylation of the anion of Piloty's acid is possible, but the structure of the alkylation product(s) has not yet been determined. It is anticipated that this will be accomplished within the next two months.

(2) Development of models for aluminum catalyzed nitrite oxidation of HEDTA (A Chalfant, undergraduate student). In simulated wastes HEDTA is cleaved by nitrite (aluminate is a necessary constituent) to ED3A, which is detected in real wastes. In earlier work[2c] C.-F. Yao determined that in acetonitrile a mixture of $[Et_4N][AlCl_4]$ and $NaNO_2$ cleaved model ßϕhydroxyethyl amines in a similar fashion (5).



(5)

These reactions were slow, presumably because of the low solubility of $NaNO_2$ in acetonitrile. One of these reactions, R_2 = -$(CH_2)_5$-, has been reinvestigated using $[Bu_4N]NO_2$, which is highly soluble in acetonitrile. Although not optimized it appears that more rapid reaction does occur. Gaseous products, which were not investigated in the earlier studies, will be determined by Ms. Chalfant during the next three months. Further NMR studies of the complexation of aluminum(III) by nitrite in acetonitrile solution[2a] will also be undertaken.

(3) Analysis of the relative contributions of thermal vs radiolytic pathways for complexant decomposition in tank 101-SY. A brief summary of the results of this analysis was given in the 1997 progress report. No further work has been done during the past 8 mon.

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

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Research Objective

One of the key issues that must be solved to achieve a successful remediation of the high level liquid wastes (HLW) at the Hanford and at Savannah River sites is the removal of the significant quantities of nitrate and nitrite in the existing liquid waste streams that are presently on these sites in the DOE

complex. One method of waste stream remediation is electrochemical oxidation, which is an in-situ method that has been well-documented to have significant advantages in many areas with respect to pump-and-treat approaches to waste remediation. There are, however, significant aspects of the electrochemical oxidation process that need to be addressed from a basic research viewpoint. The research to be performed under this proposal will investigate new materials, initially based on degenerately-doped titanias, for use in the electrochemical degradation of organics and nitrogen-containing compounds in sites of concern to the DOE remediation effort.

Research Progress and Implications

This report summarizes work after 1.5 years of a 3-year project. Progress has been made in two main areas of work. First, significant effort has been made in synthesis and characterization of new anode materials for electrochemical remediation purposes. Secondly, these materials have also been characterized as photoanodes for photoelectrochemical activity and remediation applications. Due to space limitations, only work in the former area is summarized here but information on the latter is of course available upon request from the PI's.

The primary focus of studies on electrochemical remediation is to develop titania-coated electrodes for use as improved anode materials for remediation purposes. Sol-gel processing methods were employed to prepare thin films (<1 μm thick) of titania on four metallic substrates: copper, aluminum, 304 stainless steel, and titanium. Stable electrodes were obtained by dip coating suspensions of titania on titanium supports. The resulting electrodes were tested in a batch reactor employing a three-electrode configuration for their ability to photodegrade formic acid (at 25 ppm as C) in 0.01 M NaCl. When these electrodes were fired at 300°C, they displayed reproducible performance when employed for three consecutive tests. The presence of dissolved salt did not inhibit the activity of the photoelectrodes at an applied potential of +0.5 V. When copper (at 25 ppm) was added to the test solution, removal of both copper and formic acid was observed, although the actual amounts removed depended on the type of cathode used (either platinum mesh or reticulated vitreous carbon) and the presence or absence of oxygen. An electrode that provided optimum performance in the batch reactor under an applied potential of +0.5 V is presently being tested in a recirculating system using a two-electrode configuration for possible treatment of mixed wastes.

For comparison, titania-coated titanium electrodes were also prepared by thermal oxidation in air. Electrodes prepared by heating at 300°C displayed almost no catalytic activity at an applied potential of +0.5 V. However, electrodes prepared at 500°C were both reasonably active (only some 25% less effective than the optimized electrode prepared by sol-gel processing) and stable for two tests at +0.5 V. Additional studies were conducted on the use of zirconia thin films, which are not photocatalytic, to passivate 304 stainless steel. Samples were tested using dynamic anodic polarization in a three-electrode cell with deoxygenated 0.05 M NaCl solution as solvent. Potentials were swept between -1.0 and +1.0 V. Electrodes were analyzed by scanning electron microscopy before and after corrosion testing. An electrode coated with zirconia and then fired at 700°C in air formed particles of iron oxide on the surface and readily corroded in the tests. Both this electrode and a coated electrode that was fired at 500°C in air displayed much higher currents during testing than did an untreated, unfired stainless steel electrode. However, an electrode that was coated with an aqueous zirconia sol and fired at 300°C in air was more resistant to corrosion than an untreated electrode. It thus appears that thin film sol-gel coatings, when fired at relatively low temperatures, can provide some protection for metallic electrodes and that these materials appear promising for the remediation application envisioned in the initiation of the work Further investigation of materials properties and optimization of the electrodes under both lab and batch reactor conditions will be undertaken during the next project period.

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

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Celia I. Merzbacher, Naval Research Laboratory

Research Objective

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

Research Progress and Implications

This report represents the results of an 18-month effort performed under a 3-year research award. Four categories of materials were studied: (1) several actual and proposed HLW glass compositions fabricated at Savannah River Technology Center (SRTC), samples of which had been irradiated to a dose of 30 MGy (1 Gy = 100 rad) to simulate -decay effects, (2) several high-iron phosphate glasses fabricated at the University of Missouri-Rolla (UMR), (3) one other model HLW glass and several simulated natural glasses which had been implanted with 160-keV He^+ ions to simulate-decay damage, and (4) an actual geological glass damaged by decays of trace amounts of contained ^{238}U and ^{232}Th over a period of 65 Myears. Among the category-1 materials were two samples of Defense Waste Processing Facility (DWPF) borosilicate glasses modeling compositions currently being used to vitrify HLW at SRTC. The ESR spectra recorded for the unirradiated DWPF-glass simulants were attributable to Fe^{3+} ions. The 30-MGy irradiation was found to change the Fe^{3+} concentration of these glasses by a statistically insignificant factor (0.987±0.050) and not to create measurable numbers of other defects.

Another glass irradiated to a dose of 30 MGy, an iron phosphate composition containing Li_2O and CeO_2 (modeling PuO_2) as the other two constituents, displayed a much larger -radiation response than the DWPF glass. Specifically, ~$2x10^{18}$ radiolytic superoxide ions (O_2^-) ions per gram were identified and quantified in this glass by ESR. This last observation, coupled with the fact that the ESR properties of even the unirradiated glass closely replicated those of an *iron-free* amorphous peroxyborate composition containing ~1 O_2^- ion for each 9 borons [1], has led to the formulation of a radical new structural model for the air-melted high-iron phosphate glasses, wherein each phosphorus ion is envisioned to be intimately associated with one O_2^- ion [2]. Since high-iron phosphate glasses (composition range ~0.2<[Fe]/[P]<0.67) have displayed many properties favorable for vitrification of phosphate-rich high-level wastes such as are present in large amounts at the Hanford site [3], most of the project effort to date has been devoted to fundamental studies of the lithium-cerium-iron-phosphate and UMR iron-phosphate glasses. The results of ESR, Mössbauer, thermal analysis, and gas-evolution studies carried out in informal collaboration with the UMR and Toyo University (Japan) are reported in [2]. Whether or not the new model based on these data is ultimately confirmed, the ESR technique has proven to be a powerful probe of magnetic structure in the iron phosphate glasses and materials crystallized there from and is expected to lead to valuable new insights concerning the suitabilities of these materials for HLW vitrification.

Those ion-implanted samples which were iron-free displayed ESR spectra attributable to radiolytic O_2^- and/or to nonbridging oxygen ions which had trapped holes. Among these, a borosilicate HLW-glass simulant containing 18 wt% Na_2O additionally displayed a sharp resonance line seeming to exhibit a signature of colloidal sodium (a discontinuity in the ESR linewidth-versus-temperature data at the melting point of Na). However, an alternative possibility still under investigation, is that the sharp line may be due to organic char present as a contaminant on the sample surfaces. ESR signal-to-noise ratios in these experiments were marginal due to the fact that only a layer ~1 μm deep of the 1-mm-thick samples suffered radiation damage. Nevertheless, a high-iron aluminosilicate glass (16.5 wt% FeO, 0% Fe_2O_3) exhibited very strong *ferromagnetic* resonance (FMR) signals of multi-domain metallic iron particles (diameters >20 nm) [4] and single- and multi-domain magnetite (Fe_3O_4) particles induced by the implantations. This result strongly suggests that HLW glasses containing large amounts of Fe^{2+} will disproportionate under the influence of decays of the contained actinides, resulting in separation of the FeO component into metallic iron and Fe_3O_4.

The 65-million-year-old glass displayed a narrow ESR signal, possibly that of O_2^-, which is believed to have resulted from decays. It was not possible to discriminate radiolytic FMR signals, if any, from those of naturally occurring magnetite in this sample.

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Planned Activities

Planned activities include ESR studies of model HLW glasses incorporating short-lived actinides fabricated over a decade ago. Samples of glasses prepared at SRTC and at Pacific Northwest National Laboratory containing ^{244}Cm (half-life 18.1 years) and ^{238}Pu (half life 87.7 years), respectively, have been promised. These will emulate the simultaneous effects of -particle and -recoil damage occurring over periods of 10^3 to 10^6 years in actual HLW glasses or 100 to 1,000 years in ^{239}Pu-containing glasses. Not only will this emulation be superior to simulation by He-ion implantation but it will also yield a 1000-fold improvement in ESR signal-to-noise ratios due to full volumetric irradiation of the samples. Searches for radiolytic alkali-metal colloids and O_2^- and O_3^- ions will be continued. Further studies of high-iron phosphate glasses will be carried out to refine models for their structure and to determine their radiation resistance, and DWPF-glass simulants irradiated to doses >>30 MGy will be investigated to obtain a statistically significant measure of the induced changes in iron valence states.

Other Access To Information

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

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Research Objective

This project seeks to understand the microscopic effects of radiation damage in nuclear waste forms. Our approach to this challenge encompasses studies of crystals and glass containing short-lived alpha- and beta-emitting actinides with electron microscopy, laser spectroscopy, and computational modeling and simulation. Much of our initial effort has focused on alpha-decay induced microscopic damage in 17-year old samples of crystalline yttrium and lutetium orthophosphates and thorium dioxide that initially contained ~1% of the alpha-emitting isotope Cm-244 (18.1 y half life) or the beta-emitting isotope Bk-249 (0.88 y half life). Studies will also be conducted on borosilicate glasses that contain Cm-244 or Am-241, respectively. Our goal is to gain clear insight into accumulated radiation damage and the influence of aging on such damage, which are critical factors in the long-term performance of high-level nuclear waste forms.

Research Progress and Implications

Amorphization previously has been thought to be the most important effect of radiation damage in crystalline and ceramic materials. Our studies show that for alpha-emitting actinide ions in certain crystalline phosphates, amorphization is not a significant effect of radiation damage. Instead, formation of microscopic cavities (bubbles) is an important consequence of alpha-decay events. This amorphization-resistant property makes orthophosphates a very attractive high level nuclear waste form. However, aggregation and mobilization of cavities (bubbles) might increase the leach rate of radionuclides and influence the long-term stability of the waste forms. Further research is needed before we can draw a final conclusion on the long-term effects of radiation damage in high level waste forms.

Our current understanding of microscopic effects of radiation damage is based on studies using analytical electron microscopy (AEM) and computer modeling of laser-induced optical spectra of phosphate samples doped with Cm-244.

Optical spectra of f-element ions in crystals provide “fingerprint” information about the local lattice structure, whereas line broadening of optical transitions between crystal-field states of different electronic multiplets within an f-configuration arises from static crystalline defects. We have developed a method for quantitative determination of local structure distortion from computer simulation of laser-induced fluorescence spectra. Crystal field spectra with resonant and non-resonant laser excitation were recorded for trivalent curium-244 ions in both lutetium and yttrium phosphate samples before and after annealing at 773 K for 12 hours. The observed inhomogeneous line width, 20 wave numbers, for both systems qualitatively indicates the absence of significant damage. In comparison, the inhomogeneous line width is typically about 200 wave numbers for trivalent Cm ions in glasses and less than 2 wave numbers in distortion-free crystals. After annealing, the inhomogeneous line width was reduced to less than 5 wave numbers which suggests that most lattice damage be removed.

Fundamental understanding of experimental results is achieved by theoretical modeling and computer simulation. Current accomplishments include crystal field calculation for trivalent curium ions in disordered lutetium phosphate and yttrium phosphate lattices, and Monte-Carlo simulation of alpha-decay induced atomic position displacements (amorphization). Simulation of structural disordering and the observed inhomogeneous spectral line broadening show that, for most of the existing trivalent curium ions in the samples of Cm-244 doped lutetium phosphate and Cm-244 doped lutetium phosphate, the average displacements of lattice ions that surround a curium ion is only about 0.8 picometer which is 0.2% of the unit cell dimension. Based on the existing model of

atomic displacement for alpha-decay induced damage, within 2 years after synthesis, the samples should be completely amorphized. Our results thus suggest that much of the alpha-decay induced lattice damage has been reversed by self-annealing mechanisms, which presently are not clearly understood.

Our AEM work on the same samples has produced consistent results and discovered a new phenomena technically more important than the amorphization effect. The electron diffraction (ED) patterns of the Cm-244 doped lutetium phosphate samples showed little evidence of crystalline amorphization. It was clearly evident in the high-resolution transmission electron microscopic (TEM) images of lutetium phosphate samples doped with 1% curium, that the lattice remained crystalline, however, numerous nanometer-sized (10-20 nm) bubbles were observed randomly embedded in the 17-year old samples. We have further observed that, when exposed to an electron beam, the embedded bubbles aggregated as a function of exposure time. This observation thus provides additional evidence that the bubbles developed from the aggregation of helium atoms that were created from alpha-decay of Cm-244, and the local lattice recovered from amorphization.

Planned Activities

Imaging of damage annealing and bubble aggregation will be conducted using in-situ TEM and ED while a sample is heated in the electron microscope by the end of December, 1998. TEM images will be taken periodically from borosilicate glass samples that contain Am-241 or Cm-244 as radiation damage develops. High-resolution laser spectroscopic and ODNMR measurements will be conducted, before December 30, 1998, on other aged samples such as Cm-244 doped thorium dioxide to compare the effects of alpha-decay damage in different materials. Laser spectroscopic experiments will be conducted periodically on borosilicate glass samples that contain Am-241 and Cm-244 at various loadings to determine electronic and structural damage. Our theoretical modeling effort will focus on the mechanisms and their contributions to the room temperature annealing of amorphization that is evident in phosphate crystals that contain Cm-244. A microscopic mode will be developed for interpretation of our experimental results.

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

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Research Objective

Site restoration activities at DOE facilities and the permanent disposal of nuclear waste generated at DOE facilities involve working with and within various types and levels of radiation fields. Once the nuclear waste is incorporated into a final form, radioactive decay will decrease the radiation field over geologic time scales, but the alpha-decay dose for these solids will still reach values as high as 10^{18} alpha-decay events/gm in periods as short as 1,000 years. This dose is well within the range for which important chemical (e.g., increased leach rate) and physical (e.g., volume expansion) changes

may occur in crystalline ceramics. Release and sorption of long-lived actinides (e.g., ^{237}Np) can provide a radiation exposure to backfill materials, and changes in important properties (e.g., cation exchange capacity) may occur. The objective of this research program is to evaluate the long term radiation effects in the materials in the near-field of a nuclear waste repository with accelerated experiments in the laboratory using energetic particles (electrons, ions and neutrons). Experiments on the microstructural evolution during irradiation of two important groups of materials, sheet silicates (e.g., clays) and zeolites (analcime), have been conducted; and studies of radiation-induced changes in chemical properties (e.g. cation exchange capacity) are underway.

Research Progress and Implications

As of the mid-2nd year of the 3-year project, experiments on the microstructural evolution during irradiation of two important group of materials, sheet silicates (mica) and zeolites (analcime), have been conducted; and studies of radiation-induced changes in chemical properties (e.g., cation exchange capacity) are underway. The main results are as follows:

2.1 Radiation effects in sheet silicates

Sheet silicates (e.g. micas and clays) are important constituents of a wide variety of geological formations such as granite, basalt, and sandstone. Sheet silicates, particularly clays, such as bentonite, may be used as near-field engineered barriers in high-level nuclear waste (HLW) repositories. Migration of radionuclides to the geosphere may be significantly reduced by sorption of radionuclides (e.g., Pu, U and Np) onto sheet silicates that line the fractures and pores of the rocks along groundwater flowpaths. In addition to surface sorption, sheet silicates may also be able to incorporate radionuclides, such as Cs and Sr, into the inter-layer sites. However, the ability of the sheet silicates to incorporate radionuclides and retard the release and migration of radionuclides may be significantly affected by near-field radiation. For example, the unique properties of the sheet structures will be lost completely if the structure becomes amorphous due to irradiation. Thus, the study of irradiation effects on sheet-structures, such as structural damage and modification of chemical properties, are critical to the performance assessment of long-term repository behavior.

Four different sheet silicate compositions, i.e., muscovite [$KAl_2(AlSi_3O_{10})(OH,F)_2$], phlogopite [$KMg_3(AlSi_3O_{10})(OH,F)_2$], biotite [$K(Mg,Fe)_3(AlSi_3O_{10})(OH,F)_2$] and lepidolite [$K(Li,Al)_3(Al,Si)_4O_{10}(OH,F)_2$], have been irradiated with 1.5 MeV Kr^+ ions between 20-1023 K using the HVEM-Tandem Facility at Argonne National Laboratory. The irradiation effects were characterized by *in situ* and high resolution transmission electron microscopy (TEM). All four micas were found to be susceptible to irradiation-induced amorphization at relatively low critical amorphization doses (D_c) (1-2×10^{14} ions/cm^2, fractions of a dpa) below or at the room temperature. D_c increased with irradiation temperature for all phases above 400 K. The critical temperatures (T_c), above which amorphization will not occur, for the four micas are all at or above 1000 K. Lepidolite was the most easily amorphized among the four micas at all irradiated temperatures with a T_c of 1300 K. Large gas bubbles (1-2 μm in diameter) were observed in a 800 keV Kr^{2+} irradiated biotite after 1×10^{15} ions/cm^2. The bubble volumes are too large to be explained by the implanted Kr-content indicating chemical decomposition has occurred.

2.2. Radiation effects in zeolites

Zeolites are often considered to have the potential for use as back-fill materials because of their ability to sorb radionuclides. Zeolite-group minerals, such as analcime ($NaAlSi_2O_6 \cdot H_2O$), are frequently found as precipitated phases on the surfaces of corroded nuclear waste glass. Zeolites which have precipitated on the reacted glass surface incorporate Cs and actinides through ion exchange reactions. Because zeolites have a high retention rate for radionuclides in the near-field, they will also be exposed to high radiation doses (α- and β- decay events). Irradiation of these phases may result in changes in the crystalline structure and properties, such as ion-exchange and sorption capacities, and may finally lead to the redistribution or release of retained radionuclides. Electron beam irradiation in a transmission electron microscope has been used to simulate the effects of ionizing radiation caused by β-particles and γ-rays.

Temperature and electron energy dependence of electron irradiation- induced damage in analcime has been investigated with 200 and 400 keV electron beams in the transmission electron microscope. The temperature range was between 300 to 673 K. The dose rate effect was studied in the range between $2x10^{17}$ to $1x10^{19}$ e^-/cm^2s. 1.5 MeV Kr^+ ion irradiation with *in situ* TEM was conducted at Argonne National Laboratory using the HVEM-Tandem Facility in a temperature range between 300 to 973 K with an ion flux of $5x10^{11}$ ions/cm^2s. At room temperature, the average amorphization dose for analcime under a 200 keV electron beam is $8x10^{19}$ e^-/cm^2, or ~$2x10^{10}$ Gy. The electron dose required for amorphization under a 400 keV beam is significantly higher ($3x10^{20}$ e^-/cm^2). This suggests that the ionization mechanism is mainly responsible for amorphization under electron irradiation because the ionization cross-section decreases with the increasing electron energy in this energy range. There was no significant dose rate effect on the amorphization dose within the dose rate range studied. However, under intensely focused electron beam, amorphization was almost instant although with the similar total doses, loss of Na was noted with energy dispersive x-ray analysis (EDS), and bubbles were quickly observed in the bright-field image regardless of the electron energy. The bubbles grow rapidly with the increasing electron dose, and they were confirmed to contain molecular water by TEM conducted below 200 K, which gave the diffraction pattern of ice and a unique diffraction contrast from the bubbles which only appeared at the cryo-temperatures. An anomalous temperature dependence of the amorphization dose was noted under electron irradiations, i.e., with increased temperature, the amorphization dose for analcime decreased, which is related to the thermal instability of the material. Amorphization of analcime was also easily achieved under Kr^+ irradiation at doses <0.1 dpa between 300 to 973 K. Collisional displacements are the main mechanism for amorphization under Kr^+ irradiation during which the energy deposition through ionization is less than 10^8 Gy.

In summary, sheet silicates and zeolites are susceptible to radiation-induced amorphization. Amorphization of these materials can be induced by either radiolysis or collisional displacement mechanisms. For analcime (zeolite), the radiation dose required for amorphization drops with increased temperature. Accompanying amorphization, bubbles are induced in both sheet silicates and zeolites under intense irradiation. Amorphization and formation of bubbles may change the sorption and ion exchange capacity of sheet silicates and zeolites as well as the release rate of radionuclides. This change has to be considered in the accessment of the long term reliability of a radioactive waste repository.

Planned Activities

Future research includes the following two general topics:

(1) Systematic study on radiation effects on the microstructure of sheet silicates and zeolites with energetic particle irradiation (electrons, ions and neutrons) and transmission electron microscopy. The study will include more phases (e.g., bentonite and silico-titanite). The effects of irradiation temperature, various irradiation sources and the dose rate on amorphization and bubble formation will be compared with the chemical composition, crystal structure of the target material to further understand the mechanisms responsible for the microstructural change. This project shall be completed by the end of 1998.

(2) Systematic study on radiation effects on the cation exchange capacity of zeolites and release rate of radionuclides (e.g., Cs and Sr). For these experiments, powdered samples of specified sizes will be irradiated with neutrons in the Ford Reactor of the Phoenix Memorial Laboratory at the University of Michigan because the available gamma source can not provide enough dose for amorphization in a reasonable time frame. Experiments on unirradiated control samples are underway, and the results from these experiments will be compared with those from the neutron irradiated samples which are expected in the Summer of 1999.

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Radiation Effects in Nuclear Waste Materials

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Research Objective

The objective of this multidisciplinary, multi-institutional research effort is to develop a fundamental understanding of radiation effects in glasses and ceramics at the atomic, microscopic, and macroscopic levels. The goal is to provide the underpinning science and models necessary to assess the performance of glasses and ceramics designed for the immobilization and disposal of high-level tank waste, plutonium residues, excess weapons plutonium, and other highly radioactive waste streams. A variety of experimental and computer simulation methods are employed in this effort. In general, research on glasses focuses on the electronic excitations due to ionizing radiation emitted from beta decay, since this is currently thought to be the principal mechanism for deleterious radiation effects in nuclear waste glasses. Research on ceramics focuses on defects and structural changes induced by the elastic interactions between alpha-decay particles and the atoms in the structure. Radiation effects can lead to changes in physical and chemical properties that may significantly impact long-term performance of nuclear waste materials. The current lack of fundamental understanding of radiation effects in nuclear waste materials makes it impossible to extrapolate the limited existing data bases to larger doses, lower dose rates, different temperature regimes, and different glass compositions or ceramic structures.

Research Progress and Implications

This report summarizes work after almost 2 years of a 3-year project. Work to date has resulted in 9 publications. Highlights of the research over the past year are presented below.

Theory, Simulations, and Modeling

A novel semiempirical methodology has been developed to model and simulate electron-hole pair formation in materials. This method determines the force contributions of the electron-hole pairs on the atoms and uses a time-dependent Hubbard model to propagate the electron-hole pair through the network. The model has been applied to crystalline and amorphous silicon and silica as test cases. In amorphous silica, the distorted bonds lead to localization of the exciton (formation of self-trapped exciton), and there is a significant amount of lattice relaxation. The force calculations indicate a preference for breaking bonds to form vacancy-interstitial pair defects, accompanied by large lattice relaxation effects. The pathways for the formation of various defects, using both the ground-state and excited-state forces and energetics, are being characterized. In addition, by coupling this methodology with other methods, it is possible to explore the formation and migration barriers of the defects. Initial calculations indicate that the migration barrier of a vacancy is lowered whenever an electron-hole pair interacts with the vacancy.

Threshold displacement energies and defect migration energies, which are not easily determined experimentally, are fundamental parameters controlling radiation effects in ceramics. Utilizing energy-minimization methodology, this project was the first to apply such methods to the determination of threshold displacement energies in ceramics, and the published results are in excellent agreement with experimental values. These methods have also been used to provide the only available estimates of displacement energies in zircon, since no experimental data are available. The recommended values are being used by several groups in order to compare different irradiation data sets. This method has also been used to show that oxygen vacancy migration in zircon occurs with an activation energy of 1.3 eV by hopping between corners of nearest silica tetrahedra. The oxygen vacancy migration energy in pyrochlore ($Gd_2Ti_2O_7$) has also been determined and is in agreement with experimental data.

Dynamic and kinetic computer simulation techniques are being developed to study and model the fundamental processes of radiation effects in crystalline ceramics over broad time scales. A kinetic Monte Carlo (KMC) simulation code for zircon has been written, and it is presently being tested. In this code, the kinetics of individual defects hopping on each sublattice are followed. Cascades used as input to the KMC code currently come from binary collision simulations. A molecular dynamics simulation code for zircon is also being developed in parallel.

Experimental Studies

Seven different glass compositions have been irradiated at four different temperatures with gamma radiation to doses equivalent to 25, 75, and 100 MGy. Characterization has been performed only on the lowest dose samples. The intermediate dose samples were only recently removed from the gamma-irradiation facility, and the highest dose samples are continuing to be irradiated. Density measurements indicate no significant changes in volume after 25 MGy. Initial spectroscopic analyses indicate only minor changes in the Raman, polarized-Raman, and FTIR spectra due to irradiation. However, significant changes are observed in the UV-VIS-NIR optical absorption spectra of the sodium borosilicate glass compositions. These radiation-induced variations display systematic dependencies on the temperature at which the gamma irradiation occurred. At this time, the changes in optical absorption are believed to originate from electronic defects.

Density, stored energy, EXAFS, XANES, and diffuse x-ray scattering measurements have been performed on Pu-containing zircon and a suite of compositionally identical Pu-doped (1 wt.%) waste glasses prepared with different a-activities by varying the Pu (239/238) isotopic ratio. The stored energy measured in this glass composition nearly the largest ever measured in a nuclear waste glass and shows no evidence for saturation. This large stored energy may be due to the much lower dose rates in these studies and could provide a driving force for enhanced dissolution. In the glasses, cations with long cation-oxygen bonds show a greater sensitivity to radiation effects. In the fully amorphous Pu-239 zircon, long-range correlations are lost and the uranium daughter is in a highly disordered site that is not in thermal equilibrium. In both the fully amorphous zircon (Pu-238 samples) and in the fully crystalline zircon (Pu-239 samples), the Pu is present as Pu(III), as opposed to the expected Pu(IV) state, and resides in a site that is very similar to $PuSiO_4$, the plutonium analog of zircon. This valence state for Pu in the zircon samples is most probably due to the reducing conditions employed during the original sintering.

The temperature dependence of amorphization in zircon and pyrochlore ($G_2Ti_2O_7$) under irradiation with different ion species has been determined. It was also found that ion-beam-induced recrystallization of fully amorphous pyrochlore occurs at 800° C under 1 MeV Kr^+ irradiation. Indentation measurements of pyrochlore irradiated with 4 MeV Au ions indicate a 15% decrease in elastic modulus and a 42% decrease in hardness. The accumulation and recovery of ion-beam-induced disorder in $SrTiO_3$ has also been studied by ion channeling methods. Preliminary analysis indicates that the total defect concentration on the Sr and Ti sublattices exhibits an exponential dependence on the annealing temperature. The recovery processes for defects on the O sublattice appear to be faster.

The mechanisms of gas bubble formation in nuclear waste glasses are being investigated by irradiation with inert gas atoms (50 keV Xe) at temperatures between 200 and 600° C. Modeling of data suggests that recoil-resolution of gas atoms from bubbles plays an important role in bubble

growth. As the implantation dose increases, bubbles grow by random gas accumulation until nearby bubbles interact and coalesce. The results also indicate that intermittent exposure to ionizing electrons retards bubble growth. A decrease in the threshold dose for bubble formation with increasing temperature indicates increasing Xe and bubble mobility.

Since single crystals of many oxides of interest are not readily available, the growth of single crystals or single crystal films has become necessary. Epitaxial films of pyrochlore ($Gd_2Ti_2O_7$) have been successfully grown, and ion-channeling measurements indicate excellent crystallinity. A x-ray diffraction system has been installed on the target chamber at the LANL ion-beam facility to provide a unique new capability for in situ investigations of ion-irradiation induced structural changes in solid matter.

Planned Activities

A paper describing the novel semiempirical methodology to model and simulate electron-hole pair formation in materials will be prepared and submitted for publication. Later this Summer, the modeling effort will begin simulations of excitons in binary silicate materials and on the energetics and dynamics of the triplet and singlet states of excitons in silica glass. Threshold displacement energies and defect migration energies will be determined for $Gd_2Ti_2O_7$. MD simulations of damage processes from displacement cascades in zircon will begin this Summer. In early FY 1999, parameter variation studies using the KMC code for zircon will be initiated to assess the reasonableness of the present simple model relative to a range of values expected for defect migration energies.

Characterization of glass samples irradiated with gamma radiation to 75 MGy will be initiated in June 1998. The higher dose samples will be removed for testing in November 1998 after receiving a dose of 150 MGy. In addition to characterization already performed, electron paramagnetic resonance (EPR) and transmission electron microscopy characterization will be performed.

In June/July of 1998, the Pu-zircons will be heat treated in air at elevated temperatures (~1500° C), and EXAFS/XANES measurements will be performed to confirm oxidation of the Pu(III) to Pu(IV). Additional analyses on the diffuse scattering data will be completed by October 1998, and the results will be submitted to a journal for publications.

Studies of defect accumulation and amorphization will be initiated on $Gd_2Ti_2O_7$ single crystal films and on polycrystalline $Gd_2Zr_2O_7$ in August 1998. Studies of defect recovery and and ionization-enhanced recrystallization will be initiated on $SrTiO_3$ at the same time. Studies of helium and oxygen bubble formation in glasses will be initiated in July 1998.

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

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Research Objective

The major objectives of this proposed investigation are as follows:

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

At the fundamental level, the effects of radiation, of transition metal ion additions, and of melting history in the case of multi-valent cations, on phase separation and crystallization behavior will be evaluated for simple glasses whose baseline behavior is characterized and understood. At the practical level, the program will determine the magnitude of the risk associated with the effects of radiation in inducing phase separation and crystallization. It will also provide approaches to ameliorating such effects through controlled complementary dopants and control of melting/processing conditions.

Research Progress and Implications

As of six months into the award we have begun work in two areas: (1) influence of g radiation on phase transformation behavior, (2) effect of valence state of multivalent ion on upon crystallization kinetics and mechanisms. For topic (1), after careful consideration, we have selected glasses in three composition families(Na_2O-SiO_2, Li_2O-SiO_2, and K_2O-SiO_2, called NS, LS, and KS) for investigation. NS glasses show a region of immiscibility from about 0 - 20 mol % N, and while NS2 only exhibits surface crystallization, compositions in the vicinity of NS show both internal and surface crystallization. KS glasses do not phase separate , but there is a region of “incipient” phase separation at compositions near 9 mol % K. LS2 glass appears to nucleate homogeneously, but the process may be complicated by metastable phase formation. It is believed that radiation bombardment could qualitatively change the phase separation behavior of these glasses. Glasses of all of these compositions have been prepared and have been cut into one cm. cubes for insertion into the gamma (Co^{-60}) irradiation facility at PNNL in May 1998. Sample holders have been designed and will be constructed in the near future. In order to study the influence of valence state on crystallization behavior we have chosen to examine the Iron-Soda-Silica (FeNS) system first. We have prepared a $5Na_2O$-Fe_2O_3-$8SiO_2$(5-1-8) glass under conditions where the iron is predominantly in the Fe^{3+} oxidation state. The crystallization behavior of this composition was investigated using two stage heat treatments. Nucleation temperatures of TN = 450°C, 500°C were selected and a development temperatures of TD = 685°C was used. Analysis of

the heated glasses only showed the development of surface crystallization. Internal nucleation could not be evoked. Needle-like crystals grew from the surface with a growth rate of approximately 50 μm/ s. A second glass batch of 5-1-8 composition was melted using iron oxalate as a source and with a mixture of H_2/N_2 gas flowing through the furnace in order to produce a glass containing predominantly Fe^{2+}. However, liquidus measurements of the two glasses indicated that very little of the reduced species was produced. As expected, the second glass did not exhibit internal nucleation either.

Planned Activities

In the next year the following activities are planned: (1) Prepare a reduced version of the 5-1-8 glass and measure its total Fe content as well as the % Fe^{2+}. (2) Examine the crystallization behavior of the reduced glass. (3) Perform structural studies and additional characterizations of the "unperturbed" glass compositions inserted into the gamma pit (to serve as baseline). (4) Melt NS glasses with small Fe concentrations and examine their crystallization behavior as a function of Fe content and oxidation state.

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

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Research Objective

The objective of this research program is to conduct the fundamental research necessary to develop an array of chemically selective sensors, based on highly selective molecular recognition agents and highly sensitive fluorescence and/or phosphorescence techniques, that can be coupled to fiber optics for remote analytical applications. These sensors will be of great value to DOE for the safe and cost-effective in situ characterization of high level waste tanks. Characterization of high level tank waste currently entails obtaining and analyzing core samples at the cost of about $1 million per sample. The ability to detect and measure specific chemicals and radionuclides directly inside a high level waste tank using a remote sensing device could result in considerable benefits with regard to both cost savings and safety issues. This multidisciplinary approach to the design of sensors will be to immobilize agents for selective molecular recognition, chosen from solvent extraction processes, in an organic polymer matrix that mimics the organic medium in an aqueous-nonaqueous extraction. In this manner the matrix will enhance both the separation and the achievement of chemical selectivity.

Research Progress and Implications

Good progress has been made in the first nine months of this project. Calix[4]bis-crown-6-ethers in the 1,3-alternate conformation have been shown to possess a high degree of selectivity for cesium over sodium (Cs/Na selectivity > 104 in selected diluents), and moderate selectivity over potassium

(Cs/K selectivity of about 102 in selected diluents). Our work has involved the preparation of a new class of calixarene-based ionophores. Of particular interest within this class of compounds are various derivatives of calix[4]arene-crown-4, -crown-5, and -crown-6 ionophores, possessing high selectivities for sodium, potassium, and cesium, respectively. Our goal is to synthetically modify the ionophore by attaching a fluorescent probe molecule to the crown ring in such a manner that fluorescence is normally quenched by photoinduced electron transfer but becomes activated upon complexation of the metal ion. The concept has been evaluated by observing the fluorescence quenching (of the naphthylene group) following Cs+ complexation of the ligand calix[4]-bis-(2,3-naphtho-crown-6). We are investigating potential fluorescence turn-on groups in simple crown ethers as a model for the behavior to be expected in calix crowns. We have investigated the fluorescence enhancement following metal ion complexation for the 9-methylanthracene derivative of dibenzo-21-crown-7. The degree of enhancement was disappointing, and we are preparing the 9-methyl-10-cyanoanthracene derivative, which is expected to show a greater signal enhancement. Other attractive fluorescence turn-on groups are under investigation. N-1-pyrenylmethyl-monoaza-18-crown-6 and N-(1-pyrenyl-4-butyl)monoaza-18-crown-6 were synthesized by the reaction of the appropriate bromo-pyrene derivatives with aza-18-crown-6. The compound with one carbon atom separating the aza nitrogen and the pyrene shows relatively weak fluorescence in the absence of metal ion complexation. In the presence of K+ the fluorescence is enhanced by a factor of 4. The derivative with four carbon atoms shows little quenching or metal ion enhancement. The rate of photoincuced electron transfer quenching is apparently very sensitive to the number of carbon atoms separating the fluorophore and the quencher.

Planned Activities

The relationship between the length of the carbon chain and the degree of quenching/enhancement for the aza-crowns and pyrene will be further investigated. Likewise the quenching observed in benzocrowns substituted with cyano anthracene will be defined. A suitable fluorescence enhancement mechanism will be established with simple crowns prior to preparing more complex calix crown derivatives. We will also begin evaluation of the polymeric organic matrix that will be used to attach the ionophores to the fiber optic including the necessity of adding modifiers. This evaluation will initially use the fluorescence quenching following Cs^+ complexation of the ligand calix[4]-bis-(2,3-naphtho-crown-6). The objective is to maximize both selectivity and loading as a function of matrix variation. When the ligands with fluorescence turn-on upon metal ion binding have been characterized in solution, studies will begin with the materials embedded in the optimized polymeric matrix. At this stage pattern recognition analysis of the response to complex solutions will begin using an array of selective ligands attached to an imaging fiber optic bundle. If appropriate, different modifiers/polymers will be utilized for different selectivities/loading. If the research proceeds as expected, the goal is to test an imaging fiber with an array of sensor sites selective for Cs, Na, and K.

Other Access To Information

Hai-Feng Ji, R.Dabestani, and G.M.Brown, “Fluorescence Probes for the Detection of Potassium Ions,” to be presented at the American Chemical Society National Meeting, Boston, MA.

Design and Development of a New Hybrid Spectroelectrochemical Sensor

Dr. William R. Heineman, University of Cincinnati

Carl Seliskar, University of Cincinnati
Thomas Ridgway, University of Cincinnati

Research Objective

A new concept for a chemical sensor that demonstrates three modes of selectivity (electrochemistry, spectroscopy, and selective partitioning) is being developed. The spectroelectrochemical sensor consists of an optically transparent electrode (OTE) coated with a selective film. Sensing is based on the change in optical signal of light passing through the OTE that accompanies an electrochemical reaction of the analyte at the electrode surface. The purpose of this new sensor is to significantly broaden the applicability of sensors to real samples by improving selectivity. The concept is to be demonstrated with a sensor for ferrocyanide in waste from tanks at the Hanford site.

Research Progress and Implications

This report summarizes work after 1 1/2 years of a 3-year project.

The novel sensor concept has been clearly demonstrated to work. The sensor prototype consisted of an OTE made of indium tin oxide coated on glass that was coated with a sol-gel derived charge-selective thin film. Attenuated total (internal) reflection (ATR) was the optical detection mode. The following goals have been achieved:

(1) Sensors for four analytes that are representative of inorganic and organic contaminants have been demonstrated with quantitative calibration plots: ferrocyanide, $Fe(CN)_{64}^{-}$; $Ru(bipy)_{32}^{+}$ where bipy = bipyridyl; $Re(DMPE)_{3}^{+}$ where DMPE = 1,2-bis(dimethylphosphino)ethane, and methyl viologen. Our success with the sensor for ferrocyanide is especially important since this is the sensor that we plan to develop for demonstration with samples of waste from tanks at Hanford with our collaborators at PNNL.

(2) The three modes of selectivity have been demonstrated using mixtures of the model analytes $Fe(CN)_{64}^{-}$, $Fe(CN)_{63}^{-}$, $Ru(bipy)_{32}^{+}$, and $Ru(CN)_{64}^{-}$. The level of selectivity imparted by each of the three sensor selectivity modes (selective coating material, electrolysis potential, and wavelength) was demonstrated.

(3) We have explored a variety of materials to make selective optical thin films that are also rugged and adhere well to the OTE surface. We have clearly shown that the selectivity properties of polymers such as Nafion and PDMDAAC, where PDMDAAC = poly(dimethyldiallylammonium chloride), and PAA, where PAA = poly(acrylic acid), and PVTAC, where PVTAC = poly(vinylbenzyltrimethylammonium chloride) can be imparted to sol-gel processed silica glass or a polymer-based host material. For example, an anion-selective sol-gel processed PDMDAAC-SiO_2 composite film and a cation-selective sol-gel derived Nafion-SiO_2 composite film have been applied to sensors and their use as sensors demonstrated with the analytes listed above.

(4) A comprehensive sensor instrumentation package has been developed to enable the use of signal averaging of repetitive optical response signals from the new sensor to achieve lower limits of detection. Improvements on the order of 100x have been demonstrated.

(5) We have made both slab and channel waveguides and have established the masking and polishing procedures to make channels of a variety of widths and depths ranging from single to multimode devices. The procedures for making channel waveguides with electrodes placed

next to the waveguide channel are currently being refined. Measurements with multimode planar waveguides coated with selective sol-gel processed thin films have shown that we can achieve about 3 orders of magnitude reduction in the limit of detection compared to our prototype multiple reflection (ATR) sensor. We have increased the versatility and portability of the sensor by operating the waveguide with a small HeCd laser (442 nm). We are also evaluating slab waveguides made of germania-doped silica top-coated with indium tin oxide as spectroelectrochemical sensors.

(6) Since the immediate application of the sensor concept will be for the detection of ferrocyanide in a highly radioactive environment, we have evaluated the effect of high doses of gamma radiation on various sensor components and found the sensor to be adequately rugged.

Planned Activities

The following work is planned for the second 1 1/2 years of the project:

(1) Evaluation of the sensor for ferrocyanide using simulant samples prepared by PNNL.
(2) Continued development of waveguides to improve detection limits and for device miniaturization.
(3) Construction of a portable sensor to test at PNNL for detection of ferrocyanide in actual samples from waste tanks at the Hanford site.
(4) Further evaluation of selectivity properties, detection limits, and ruggedness of sensors.
(5) Evaluation of extension of the sensor concept to other analytes of DOE interest.

Other Access To Information

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11. Evaluation of the Electrochemical Characteristics of a Poly(vinylalcohol)/poly(acrylic acid) Polymer Blend, C.O. Dasenbrock, T.H. Ridgway, C.J. Seliskar and W.R. Heineman, Electrochim. Acta, in press (1998).
12. Dual Analyte Spectroscopic Sensing in Sol-Gel Derived Polyelectrolyte-Silica Composite Thin Films, Yining Shi, C.J. Seliskar and W.R. Heineman, Talanta, in press (1998).
13. Formulation, Characterization and Sensing Applications of Transparent Poly(vinyl alcohol)-Polyelectrolyte Blends, L. Gao and C. J. Seliskar, Chem. Materials, submitted 3/25/98.

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

Dr. Digby D. MacDonald, Pennsylvania State University

Research Objective

Objective of this project is to develop and use Electrochemical Emission Spectroscopy (EES) and other electrochemical techniques as in situ tools for exploring corrosion mechanisms of iron and carbon steel in highly alkaline solutions and for continuously monitoring corrosion on structural materials in DOE liquid waste storage system. In particular, we will explore the fundamental aspects of the passive behavior of pure iron since breakdown of passivity leads to localized corrosion.

Research Progress and Implications

This report summarizes work after 1 year of a 3 year project

During the past eight decades the passive film on iron has been the subject of numerous investigations [1-7] aimed at developing a detailed understanding of the film growth mechanisms, the film structure and composition as well as reduction of iron oxides that form on the surface. In most of this work, the results have been interpreted by assuming the presence of a two-layer film consisting of an inner layer of Fe_3O_4 and an outer layer of g-Fe_2O_3. This is based on a frequently reported observation of two reduction waves in galvanostatic and potentiodynamic experiments. Those two waves (or peaks) are generally attributed to reduction of first, the outer layer and then second, the inner layer to form soluble Fe^{+2} [8-9]. An alternative explanation can be found in the proposal that the film is a single layer of g-Fe_2O_3. In this case, the two reduction waves are believed to be the reduction of Fe_2O_3 first to Fe_2^{+} and then to Fe0 [10,11].

Electrochemical studies were carried out in a three electrode PTFE electrochemical cell. The counter electrode was a Pt wire and all potentials were measured against a saturated calomel electrode (SCE). The working electrode was a pure iron wire (> 99.99%) with a diameter of 1 mm. The wire was embedded in a two component epoxy resin and mounted in a PVC holder. The samples were mechanically polished with 1200 grit emery paper and with 0.3 mm Al_2O_3, then rinsed and sonicated in distilled water.

All experiments were performed at ambient temperature (22 – 25°C) in pH 8.4 borate buffer (0.075 M $Na_2B_4O_7$* 10 H_2O, 0.3 M H_3BO_3), which was dearated with N_2 during the measurements. Prior to all experiments, the samples were cathodically polarized at –1.0 V SCE for 5 min. to remove the air formed film. Then the potential was stepped (within 0.02 s) to different formation potentials (ranging from 0.0 V to 0.6 V). The potential was maintained constant until a steady-state was achieved (typically between 24 and 48 hr).

In some experiments, 0.01 M EDTA was added to the solution in order to hinder the formation of the precipitated layer. Formation of passive films consisting only of barrier layer, is vital to our experiments since the current models describing passivity breakdown take into account the existence of only the barrier layer.

On cyclic voltammograms of Fe in borate buffer solution with and without EDTA, the active dissolution current is higher , and the passive current is lower in the presence of EDTA. On reverse scanning, the current recorded in borate buffer with EDTA becomes cathodic at more noble potentials (around 0.0 V SCE) whereas without EDTA the current becomes cathodic at potentials around –0.2 V SCE. In potentiostatic experiments, in the presence of EDTA, the current decay is slower than without EDTA (suggesting lower film formation rate), but after approximately 15 hr the passive current on Fe is lower than that in the solution without EDTA. In order to study the influence of EDTA in hindering the formation of the outer layer, galvanostatic and potentiodynamic reduction

curves were measured. The samples were passivated for 60 hr at 0.6 V SCE. In galvanostatic reduction experiments, the reduction current density was –25 mA/cm^2. In the case of potentiodynamic measurements, the potential sweep rate was –1mV/s. Particularly from the potentiodynamic curves, it is obvious that the film reduction process in borate buffer solution occurs in two steps – as reported several times in the literature, which can be attributed to the Fe^{+3}/Fe^{+2} reduction in the outer g- Fe_2O_3 layer as well as in the inner Fe_3O_4 part of the film. The potentiodynamic curve recorded in borate buffer with EDTA solution displays only one reduction peak suggesting the reduction (and hence the existence) of only a single layer passive film.

It is well known that passive films on most metals and alloys exhibit a semiconducting behavior. Therefore, in recent years a variety of experimental techniques have been applied to studying the electronic properties of passive films. The most common in situ method for probing the electronic properties of passive film is (besides photoelectrochemistry) Mott-Schottky analysis (capacitance measurements).

In Mott – Schottky experiments, the specimens are passivated for at least 24 hr at different formation potentials and the imaginary part of the impedance (Z") at 1 kHz is recorded as a function of the potential. The interfacial capacitance, C, is obtained from C = -1/wZ". According to Mott – Schottky theory, the space charge capacitance of a semiconductor is given by a well know equation [12] where C-2 is inversely proportional to the donor concentration (for an n-type semiconductor). Thus, for C-2 vs. V profiles which display linear part, the calculation of the number of defects (which serve as charge carriers) in the passive film is straightforward.

Assuming that the capacitance of the Helmholtz layer can be neglected, C = Csc.

C-2 vs. V profile recorded for passive film formed on Fe in borate buffer solution with and without EDTA show non-linear behavior. The observed nonlinearity can be due to several phenomena, such as an inhomogeneous doping profiles, the presence of deep states, and the presence of surface states, which become ionized as the Fermi potential changes. The ionized states then contribute to the measured charge. The doping concentration can be determined from the slope of the linear part of the curve in the relevant potential range. It is obvious that the passive film formed on iron in borate buffer solution is less defective than that formed in the presence of EDTA. This phenomenon may be due to the lower thickness of the passive films formed in borate buffer solution with EDTA, because of the higher dissolution rate of the film. The donor densities calculated for all formation potentials for passive films formed on iron decrease with increasing voltage (over the range of 8.8 to 5.2 * 1020cm-3). The Mott-Schottky plots were also measured as a function of a potential sweep rate. For two different potential sweep rates 1 mV/s and 0.2 mV/s the recorded C-2 vs. V profiles were virtually the same.

Steady – state thicknesses of the films formed at different potential were calculated from the measured capacitance. The results display a linear dependence between the film thickness and formation voltage above 0.4 V SCE. Film thickness for formation potentials below 0.4 V SCE is constant and equals 2.3 nm. This result may suggest the existence of an additional capacitance, Cadd, which is smaller than that of oxide, (Cox). Accordingly, for potentials more negative than 0.4 V SCE this additional capacitance governs the overall measured capacitance,C (1/C = 1/Cadd + 1/ Cox). EIS measurements seem to confirm this hypothesis; for films formed below 0.4 V SCE there is an additional capacitative loop observed in the impedance locus at high frequencies.

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Planned Activities

In the future, we intend to continue our work on studying the passivity of metals in alkaline solutions including investigation of the electrochemical behaviors of Ni and Cr. This task will continue during next year.

The NO_x System in Nuclear Waste

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Dr. Don Camaioni, Pacific Northwest National Laboratory

Research Objective

The objective of this project is to assist EM sites in the resolution of outstanding safety issues involved in the temporary storage of high-level waste (HLW) in large tanks. To achieve this objective, mechanisms of the radiolytic and radiolytically induced processes that occur in the waste are quantitatively studied. The information is incorporated into a computer modeling of the tanks chemistry under various scenarios and the predicted results are rapidly conveyed to the site operators.

Research Progress and Implications

This report summarizes the technical achievements of a 3-year project that is now in its 2nd year of operation. The project is a collaborative effort between the ANL and PNNL and is strongly coupled to another EMSP project ("Interfacial Radiolysis Effects in Tank Waste Speciation" PI: T. Orlando, PNNL) and to the safety programs at the Hanford site ("Organic Tanks Safety Program: Waste Aging Studies", PI D. Camaioni, PNNL). Information from the project is also shared directly with Westinghouse Savannah River personnel. In general, the basic studies are performed at ANL and PNNL and the information is continuously shared with Tanks Safety Programs. To further facilitate the exchange of information and the immediate incorporation of results into operations, we conducted at least twice a year "coordination meetings" at the various laboratories where the site operators (e.g. from DE&SH, Numatec, WSRC, etc.) participate, both to present their needs and to obtain updated information.

We have shown that, even at concentrations relevant to HLW, the yields of the primary reducing radicals of the NO_x family are not altered significantly. Most primary radicals that results from the irradiation of water in highly concentrated waste simulants are rapidly converted to NO_2 radicals, and to a lesser degree to NO radicals. We determined quantitatively the rates of the major reactions involved in these conversions. An important intermediate in that conversion is the short-lived NO_{32}^- radical, obtained from the reaction of e-aq and its precursors with nitrate. We determined the redox potential of this species (i.e., of the couple NO_3-/NO_{32}^-) across the whole pH range. We also determined the analogous redox potential for the nitrite species (i.e. of the couple NO_2^-/NO_{22}^-). The results show that electron transfer from the nitrate di-anion to nitrite is thermodynamically favorable, but kinetically the reaction is sluggish. We believe, and kinetic modeling of the tanks chemistry seems to require it as well, that this reaction, $NO_{32}^- + NO_2^- \rightarrow NO_3^- + NO_{22}^-$, occurs in the tanks with an efficiency that is determined by the nitrite concentration. The implication of this important conclusion is that the chemistry in the tanks may be diverted from NO_2 to NO radicals at a [nitrite] dependent efficiency. Whereas NO_2 provides facile pathways to organic degradation, NO provides pathways for N_2O generation. The NO_2 radical is important to the resolution of the organic tanks issue and NO, and subsequently N_2O, is an important component of the flammable gas issue.

The primary radical, which oxidatively degrades the organic molecules in the waste tanks, is suspected to be NO_2. To independently verify the identity of the major oxidizing radical, we compared radiolytic degradation results with results from degradation caused by genuine NO_2 gas. We contacted aqueous alkaline solutions of organic species with gaseous NO_2 IDA>Gly>formate were determined by competition experiments in which each of the aminocarboxylates was oxidized in the presence of formate-^{13}C to obtain initial production rates of formate-^{12}C and carbonate-^{13}C. Similar reactivity patterns were obtained in both the radiolytic and NO_2 contact approaches.

Using methodologies based on conductivity changes that we developed in the 1st year of our project, we recently measured rate constants of reactions of organic radicals of model HLW compounds with NO_2^- (nitrite) and with NO_2. For the NO_2 radicals, two possible pathways were identified: a) Electron transfer to form nitrite, and b) Radical combination to form nitro-organic moieties. The latter pathway (b) occurs either via the O or the N atoms at nearly equal probabilities. The O - ester hydrolyzes to produce nitrite.

Reaction rates of the same organic radicals with nitrite (NO_2^-) were also measured. We find that electron transfer is a leading pathway and it becomes faster as the pH drops. This reaction is important in the tanks chemistry because it generates a carbonyl product on the organic side (e.g.. aldehyde that may proceed to thermally generate H_2) and NO from nitrite. As discussed above, the latter provides another route for production of N_2O.

We also attempted to determine the effect of particulate material in the waste composition on radiolytic yields. Yields of reducing radical at increasing concentrations of silica particles were measured. We find that if the particles are small enough (largest sizes measured were 22 nm in diameter) the concentration of reducing radicals actually increases. This is an observation of exceptional importance and direct relevance to the tanks chemistry, as well as to long term storage in waste forms other than glass (e.g., grout, saltstone etc.). Long term storage in a matrix composed of small particles may defeat the purpose of the matrix. It may “channel” the radiation energy into the small quantities of water that are present in the matrix pores. This effect may lead to very efficient radiolysis of water, along with its adverse effects. In tanks, it may lead to preferential generation of gaseous products in the vicinity of solid particles. This, in turn, favors attachment of gas bubbles to the solid particles, thus contributing to the gas retention problem. It may also alter the chemistry that prevails in tanks with floating organic layers following tank draining operations. As the aqueous phase is depleted, and the organic layer comes into contact with the solid-rich sludge phase, the enhanced deposition of energy in the vicinity of the particles may trigger enhanced organic radiolysis.

Planned Activities

We will continue our studies of NO_2-radical chemistry and the effects of particles on radiolytic yields. We will study in detail the reaction mechanisms of amine-containing multi-functional molecules with NO_2, and will extend these studies to glycolate and acetate, which are known to be present in the HLW. These are model compounds for the chelators that are prevalent in the tanks’ HLW. Since the chelators, their model compounds, and their degradation products, all contain at least three potential points of attack by the radical, -N-H, -C-H and -CO_2^-, the point of attack will determine the fate of the organic compound. We will also establish an absolute rate scale for these oxidation reactions that are presently determined only on a relative scale. In the study of the effect of particles on radiolytic reactions we will turn our attention to the fate of holes. Do they migrate to the aqueous phase, similar to the electrons, or do they remain in the solid and/or its surface?

We expect to provide absolute rate constants for NO_2 reactions with the relevant organic molecules by the end of next year (i.e. end of the present grant award). This will allow incorporation of much of the data into a computer model of the tanks chemistry. On the same time scale, we will also determine if radiolytically generated holes, in silica particles of various sizes, migrate out of the solids into the aqueous phase. This may have major consequences to oxidative degradation of organics in the tanks and may impact other EMSP projects as well (e.g. “Ionizing Radiation Induced Catalysis on Metal Oxide Particles,” PI: T. Fryberger). We will organize at least two more “coordination meetings” during the lifetime of the project to enhance dissemination of the knowledge generated and its incorporation into operations.

Other Access To Information

We disseminate our results directly to the Hanford and Savannah River sites in periodic reports and during internally organized "coordination meetings" with selectively invited site operator entities. Below is a list of formal publications and presentations:

Publications

1. "Charge Carrier Transfer Across The Silica Nanoparticle / Water Interface," T. Schatz, A.R. Cook and D. Meisel, J. Phys. Chem., Submitted for publication
2. "Reducing Radicals In Nitrate Solutions. The NO_{32}- System Revisited," A.R. Cook, N. Dimitrijevic, B.W. Dreyfus, D. Meisel, L.A. Curtiss and D.M. Camaioni, J. Phys. Chem., Submitted for publication
3. "Chemistry, Radiation, And Interfaces In Suspensions Of Nuclear Waste Simulants," D. Meisel, A. Cook, D. Camaioni, and T. Orlando, in "Photoelectrochemistry", Ed. K. Rajeshwar, L.M. Peter, A. Fujishima, D. Meissner, M. Tomkiewicz, The Electrochemical Society Pub., Vol. 97-20, 350-7 (1997)

Presentations

1. "Radiation and Chemistry in the Management of Nuclear Waste. Radicals, Particles, and Interfaces" D. Meisel, Invited Lecture, "Research Needs and Opportunities in Radiation Chemistry", DOE-ER/BES Workshop, Chesterton, IN, April 19-22. 1998
2. "Radiation and Chemistry in the Nuclear Arena: Radicals, Particles and Interfaces," D. Meisel, Seminar, University of Notre Dame, Notre Dame, IN, April 2, 1998
3. Science and Technology in the Management of Nuclear Waste, D. Meisel, Water Program, University of Wisconsin, Madison, WI, November 6, 1997
4. "Some Fundamental Studies on the Effects of Radiation and Interfaces in High Level Wastes," D.M. Camaioni, D.M., K. Knutsen, J.C. Linehan, T.M. Orlando, A. Cook, and D. Meisel, Symposium on Future Directions in Radioactive and Mixed Waste Management, Annual Meeting, Am. Chem. Soc., Las Vegas, NV September 7-11, 1997.
5. "The Radiation Chemistry of the NOx System Revisited" A.R. Cook, L.A. Curtiss, B. Dryefus, D. Camaioni and D. Meisel, Symposium on Future Directions in Radioactive and Mixed Waste Management, Annual Meeting, Am. Chem. Soc., Las Vegas, NV September 7-11, 1997.
6. "Interfacial Charge Transfer in Irradiated Suspensions. Implications to Nuclear Waste." T. Schatz, A.R. Cook and D. Meisel, Symposium on "Actinide Solution Chemistry", Annual Meeting, Am. Chem. Soc., Boston, MA, August 23-27, 1998

Interfacial Radiolysis Effects in Tank Waste Speciation

Dr. Thomas M. Orlando, Pacific Northwest National Laboratory

Don Camaioni, Pacific Northwest National Laboratory
Dan Meisel, Argonne National Laboratory

Research Objective

The purpose of this program is to deliver pertinent, fundamental information that can be used to make technically defensible decisions on safety issues and processing strategies associated with storage and clean up of DOE mixed chemical and radioactive wastes. The radioactive and chemical wastes present in DOE underground storage tanks contain complex mixtures of sludges, salts, and supernatant liquids. These "mixtures," which contain a wide variety of oxide materials, aqueous solvents, and organic components, are constantly bombarded with gamma quanta, beta and alpha particles produced via the decay of radioactive isotopes. Currently, there is a vital need to understand radiolysis of organic and inorganic species present in mixed waste tanks because these processes: *a) produce mixtures of toxic, flammable, and potentially explosive gases (i.e., H_2, N_2O and volatile organics) b) degrade organics, possibly to gas-generating organic fragments, even as the degradation*

reduces the hazards associated with nitrate-organic mixtures, c) alter the surface chemistry of insoluble colloids in tank sludge, influencing sedimentation and the gas/solid interactions that may lead to gas entrapment phenomena.

Research Progress and Implications

This report summarizes the technical achievements of a 3-year project that is now in its 2nd year. Progress in three areas is reported: 1) radiation effects at $NaNO_3$ crystal interfaces, 2) reactions of organic complexants with NO_2 in water, and 3) radiation effects in oxide particles. The research disclosed in this report is the result of collaborations between the listed investigators, who closely coordinate their efforts on this project, another EMSP project located at ANL ("The NO_x System in Nuclear Waste," PI: D. Meisel) and a project in the Tank Waste Safety Program at the Hanford Site ("Waste Aging Studies Project," PI: D. M. Camaioni).

Radiation Effects at Crystalline $NaNO_3$ Interfaces: The low energy (5-100 eV) electron-stimulated desorption (ESD) of neutrals from $NaNO_3$ single crystals is compared with our previous state-resolved 193 nm (6.4 eV) photon-stimulated desorption (PSD) study. The PSD study demonstrated that excitation of $NaNO_3$ interfaces with 193 nm photons (6.4 eV) results in the stimulated desorption of predominantly NO(^{2}?) and O(^3P_J). The 6.4 eV valence band excitation in $NaNO_3$ solids/interfaces has been correlated with the $NO_3^-\pi^*\leftarrow\pi$ band, and is below the nominal band gap energy of ~8 eV. Excitations of this band create localized excitons, which couple to phonons and trap at surface and/or defect sites. Decomposition of these excitons results in the direct desorption of both thermal and non-thermal NO($^2\Pi$) and O(^{3}P).

The controlled low-energy electron-beam irradiation studies carried out in this EMSP program also demonstrate that NO($^2\Pi$) and O(^3P_J) are the primary direct neutral desorption products. In addition to NO and O, some O_2(g) and NO_2(g) are produced from both 100 eV ESD and 193 nm PSD. Unlike NO and O, we believe that O_2(g) and NO_2(g)are produced indirectly and do not represent direct products of $NaNO_3$ radiolysis. In fact, the NO_2 data are well fit by a Maxwell-Boltsmann distribution at the $NaNO_3$ surface temperature of 423 K, indicating interaction with the surface prior to desorption. In contrast, both the O and NO velocity distributions are *non-thermal*, with a significant portion of their populations "hotter" than the $NaNO_3$ surface temperature. The product yields and NO($^2\Pi$) and O(^3P_J) velocity distributions obtained from ESD and PSD are essentially identical. Therefore, the final states involved in ESD and PSD must be similar. *This is an important result since it allows us to initiate "radiation" induced processes at $NaNO_3$ interfaces by selectively exciting the $NO_3^-\pi^*\leftarrow\pi$ band.*

We conclude from these experiments that the primary direct radiolysis products of $NaNO_3$ solid surfaces are NO, O, and O^-(sf). Secondary (indirect) radiolysis products are O_2 and NO_2. The latter are formed below the surface in the bulk crystal, but may diffuse to the surface and react with interfacial species. The generation of strongly oxidizing radicals, O and O^-, and NO at $NaNO_3$ interfaces is important since organic radicals generated at the interface can react with NO to produce nitrogen-containing organic species. The decay of these species can lead to the production of HNO (NO^- in aqueous conditions) which can undergo recombination reactions and directly yield N_2O(g). The importance of this interfacial reaction pathway is currently being investigated by controlled electron-beam induced radiolysis of $NaNO_3$ surfaces containing multilayers of CH_3OH. Methanol radicals, $HOCH_2$• and CH_3O•, are generated from both direct interactions of CH_3OH with energetic electrons and reactions with oxidizing radicals, O and O^-(sf), That are generated by electron impact of the nitrate interface. The methanol radicals are expected to react with NO that is generated concurrently by electron impact of the nitrate interface. These reactions should produce N_2O, or its precursor, as well as other compounds that may degrade to nitrogenous and H_2 gases in tank wastes.

Reactions of Model Organic Complexants with NO_2 in Water: Radiolysis of homogeneous aqueous waste solutions generate primarily OH/O^- and NO_2. Since nitrite concentrations are high in aqueous wastes, a significant fraction of the O^- generated at the solution crystal interfaces will probably convert to NO_2. Therefore, reactions of NO_2 with organic species in solution are being studied. Though NO_2 is one of the dominant oxidizing radicals generated by radiation effects on nuclear waste, there

is little knowledge of its reactions with organic compounds that were used in nuclear materials processing and stored in waste tanks. Waste aging studies have been performed at the Hanford Site to explain waste characterization data and predict effects of organic aging on the potential combustion hazards of organic containing nitrate-rich wastes. These studies simulated waste aging by gamma-irradiating non-radioactive waste simulants. We are performing complementary experiments in this EMSP project to verify the role of NO_2 and to elucidate reaction kinetics and products for development of mechanistic kinetic models. The experiments contact aqueous alkaline solutions of organic species with N_2 containing <100 ppm NO_2. The NO_2 dissolves in the solutions and hydrolyzes competitively with reduction by organic solutes. Preliminary experiments have surveyed the reactions of nitrilotriacetate (NTA), iminodiacetate (IDA), glycine, and formate. Products were analyzed using ^{1}H and ^{13}C nuclear magnetic resonance spectroscopies and ion chromatography. The results show that NTA degrades via stepwise dealkylation giving mainly formate, carbonate and oxalate. Formate degrades to carbonate when reacted with NO_2, but at a slower rate. Relative reactivities from competition experiments show NTA>IDA>glycine>formate. We note that very similar results have been obtained in Hanford Waste Aging Studies that irradiated simulated waste solutions that contained these compounds. Therefore, the NO_2 contact experiments appear to corroborate our view that NO_2 is a dominant species responsible for radiolytic oxidation of organic chemicals in DOE tank wastes at Hanford and Savannah River sites.

Radiation Effects in Oxide Particles: To begin studying radiation chemical effects in solutions containing colloidal oxide particles, pulsed radiolysis studies of silica-loaded aqueous solutions were carried out at ANL. These pulse radiolysis studies indicate that absorption of the radiation in the solid particles may lead to the transfer of charge across the particle-liquid interface and initiate chemistry at the interface and in the surrounding solution. Since the fraction of energy (ionizing radiation) absorbed by the particles increases with loading, this observation suggests that the absorption of radiation by the solid particles causes electrons to be ejected into the surrounding solution. If the radiation effects were localized within silica particles, the yield of solvated electrons should decrease. Instead, the yields follow the average sample densities that are calculated from particle concentrations and the density of silica. The results have many practical implications. For high level radionuclides stored in suspensions in large tanks, the presence of the particles will promote generation of water radiolysis products (of particular concern is H_2) in the vicinity of the particles. This may increase the probability of retention of products near the particles, e.g. by gas-bubble attachment to the particle, and may lead to serious safety concerns.

Concluding Statements: *The implication to tank waste chemistry of the above research on interfacial radiolysis effects is that radiation absorbed by solid waste components ($NaNO_3$ crystallites and metal oxide particles) will result in chemistry at waste interfaces and in solution phases.* Therefore, heavily solids-laden wastes may contribute, not deter, radiolytic aging. Radiolysis of both the solid and liquid-phase clearly contribute to the production of species which are involved in the generation of gases such as H_2, N_2O and NH_3.

Planned Activities

The project will continue activities in the above areas. At PNNL, radiolytic processes occurring at $NaNO_3$ crystal interfaces with organic overlayers will be studied using ESD techniques. Initial experiments will condense thin layers of methanol on a $NaNO_3$ crystal and irradiate with 100 eV electrons. Then, the crystal will be slowly warmed to desorb the organic layers into a mass spectrometer to detect and identify products. Experiments will also start studies of solutions using a novel apparatus that inject beams of liquids into a vacuum chamber where the beams are irradiated and radiolysis products are detected using mass spectrometers and sensitive laser diagnostics. Solutions to be studied will include aqueous $NaNO_3$ and metal oxide colloids. In collaboration with the ANL EMSP project, "The NO_x System in Nuclear Waste," we will continue studies to elucidate mechanisms of NO_2 oxidations of organic complexants and measure relative rate constants using a reactive dissolution apparatus that passes dilute (ppm) concentrations of NO_2 through aqueous solutions of substrates. Substrates targeted for study include aminocarboxylates, glycolate, acetate, and formate. At ANL,

studies of the effects of particles on radiolytic yield will continue. Attention will focus on the fate of holes that are initially generated in the particle. The research will try to determine if they migrate to the aqueous phase, similar to the electrons, or remain on the solid and its surface.

Other Access To Information

This project and the ANL EMSP project, "The NO_x System in Nuclear Waste," are strongly coupled with the "Waste Aging Studies" project at the Hanford Site such that the basic studies are performed at ANL and PNNL and the information is continuously shared with the Tank Waste Safety Program. Information from the projects is also shared directly with Westinghouse Savannah River personnel. To further facilitate the exchange of information and the immediate incorporation of results into operations, we conduct at least semi-annual "coordination meetings" in which the site operators (e.g. from DE&SH, Numatec, WSRC, etc.) participate both as contributors and observers. In addition, we participate in national and international meetings of scientific societies, e.g. the American Chemical Society, the Electrochemical Society, and the American Physical Society.

Program Publications and Presentations

"Chemistry, Radiation, and Interfaces In Suspensions Of Nuclear Waste Simulants," D. Meisel, A. Cook, D. Camaioni, and T.M. Orlando, in "Photoelectrochemistry", Ed. K. Rajeshwar, L.M. Peter, A. Fujishima, D. Meissner, M. Tomkiewicz, The Electrochemical Society Pub., Vol. 97-20, 350-7 (1997).

"Low-energy (5-100 eV) Electron and Ultraviolet (6.4 eV) Photon-stimulated Desorption of Neutral Fragments from $NaNO_3$ Single Crystals," K. Knutsen, and T.M. Orlando, *Appl. Surf. Sci.* in press.

"Charge Carrier Transfer Across The Silica Nanoparticle/Water Interface," T. Schatz, A. R. Cook, and D. Meisel, *J. Phys. Chem*., Submitted for publication

"Quantum-Resolved Studies of Electron-Stimulated Processes in Wide Band-Gap Materials", T.M. Orlando, M.T. Sieger , W.C. Simpson, and K. Knutsen, International Conference on Desorption Induced by Electronic Transitions (DIET) VII, Ambleside UK, April 8-11, 1997.

"UV Photon- and Low-Energy (5-100 eV) Electron-Stimulated Processes at Environmental Interfaces", T.M. Orlando, M.T. Sieger, W.C. Simpson, D.P. Taylor, and K. Knutsen, The 24th IEEE International Conference on Plasma Science, San Diego, CA, May 19-22, 1997.

"A Comparison between UV-Photon and Low-Energy Electron-Stimulated Desorption Processes from Wide Band-Gap Materials", T.M. Orlando, D.P. Taylor , W.C. Simpson, and K. Knutsen, The Fourth International Conference on Laser Ablation, COLA '97, Monterey, CA July 21-25, 1997.

"Some Fundamental Studies on the Effects of Radiation and Interfaces in High Level Wastes," D.M. Camaioni, D.M., K. Knutsen, J.C. Linehan, T.M. Orlando, A. Cook, and D. Meisel, Symposium on *Future Directions in Radioactive and Mixed Waste Management*, 214th ACS National Meeting, Las Vegas, NV September 8, 1997.

Colloidal Agglomerates in Tank Sludge: Impact on Waste Processing

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Research Objective

Insoluble colloidal sludges in hazardous waste streams such as tank wastes can pose serious problems for waste processing, interfering with retrieval, transport, separation, and solidification procedures. Properties of sediment layers and sludge suspensions such as slurry viscosities, sedimentation rates, and final sediment densities can vary by orders of magnitude depending on the particle types present, the degree to which the particles agglomerate or stick to each other, and on a wide range of processing

parameters such as solution shear rates, pH, salt content, and temperature. The objectives of this work are to:

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

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2) determine how agglomeration phenomena influence physical properties relevant to waste processing including rheology, sedimentation, and filtration; and
3) develop strategies for optimizing processing conditions via control of agglomeration phenomena.

Research Progress and Implications

This project summarizes work performed after almost two years of a three year project. Significant findings include:

Particles in Actual Tank Wastes - Transmission electron microscopy of actual wastes shows that most sludges consist of agglomerates of submicron ($< 10^{-6}$ m) primary particles of hydrated oxides and insoluble salts. Model colloid suspensions for this work were selected to duplicate the compositions and particle morphologies in actual waste.

Agglomeration of Primary Particles - Static light scattering measurements on both model suspensions and actual wastes show that in the basic salt solutions found in most tank wastes, primary particles undergo extensive aggregation to form fractal agglomerates. The fractal nature of the agglomerates has an enormous impact on slurry properties because fractal objects occupy much more space than dense objects at the same solids loading.

Effect of Agglomeration on Slurry Viscosity - The viscosities of both simple suspensions and actual wastes can vary by over five orders of magnitude (1 centipoise to over 10,000 centipoise) depending on the extent of agglomeration and solids loading. Slurries can exhibit Newtonian (viscosity independent of shear rate), shear thinning (viscosity decreasing with shear rate), or shear thickening (viscosity increasing with shear rate) behavior. The most viscous suspensions contain agglomerates of submicron particles. To achieve desired viscosities for retrieval and transport, sludges of such particles may have to be diluted by a much as a factor of twenty, producing enormous quantities of wastes.

Effect of Agglomeration on Sedimentation - Measurements on simple suspensions and on actual wastes show that sedimentation rates can vary by over three orders of magnitude (from no measurable sedimentation to over 30 cm/hr) depending on primary particle and agglomerate sizes. Measurements on actual wastes indicate that in lab scale tests, final sediment densities of from 1-8 vol% are common. This means: 1) that particulate layers will occupy large processing volumes during steps such as sludge washing and leaching, and 2) that the volume occupied by sediment layers is predominantly interstitial water which cannot be removed during solid-liquid separations.

Effect of Salts on Agglomeration and Sedimentation - Experiments on small gibbsite particles indicate that the solids loading in the sediment layer is highly dependent on the degree of agglomeration and the interparticle interaction potential. If particles are dispersed, particle packing is highly efficient

(up to 50 vol%). For agglomerated systems, sediment densities can be increased by as much as a factor of three by weakening interparticle interactions, which increases the compressibility of the sediment. The sediment compacts under its own weight. Experiments have shown that in the high-salt regime of most tank wastes, sediment densities decrease, then increase with salt content due to the interplay of electrical double layer and hydration forces. The presence of calcium and other divalent cations is particularly effective in promoting sediment compression. Salts such as apatite also appear to promote compression by disrupting hydrogen bonding between hydrated oxide particles. Manipulation of such forces could be used to improve tank utilization and the efficiency of solids-liquids separations during steps such as sludge washing and leaching by as much as a factor of four.

Planned Activities

While work done so far in FY98 suggests that short range forces are important in controlling the properties of tank sludge, quantitative models do not yet exist to predict sludge properties such as sediment densities or slurry viscosities based on interaction potentials. Work in FY99 will focus on the following tasks aimed at developing quantitative models for sludge properties based on tank waste processing chemistry:

Measurement of Short Range Forces - Interaction potentials will be measured between surfaces relevant to tank waste disposal using a surface forces apparatus.

Measurement of Agglomerate Sized and Structures - Small-angle x-ray scattering (SAXS) and light scattering will be performed on model suspensions in both static and sheared solutions to determine how different salts influence the fractal dimension and size of agglomerates of submicron particles.

Modeling of Agglomerate Properties - Computer codes developed at PNNL and SNL will be used to calculate the kinetics of aggregation, provide information regarding agglomerate sizes and structures, and calculate the ease of deformation of agglomerates as a function of the magnitude of interparticle interaction potentials.

Once the framework relating interparticle forces, agglomeration, and sludge properties is established, the project will shift to deliberate modifications of sludge suspensions to optimize properties for retrieval, transport, and sedimentation processes.

Other Access To Information

B.C. Bunker, J. Liu, D.R. Rector, G.L. Graff, P.A. Smith, P.J. Bruinsma, L. Song, X.S. Li, J.D. Virden, N.G. Colton, J.R. Philips, K.D. Keefer, and J.M. Tingey, “Fractal Colloidal Agglomerates in Nuclear Tank Wastes: Impact on Waste Properties and Processing,” submitted to Science

V.S. Stenkamp and J.C. Berg, “The Role of Long Tails in Steric Stabilization and Hydrodynamic Layer Thickness,” Langmuir, 13, 3827 (1997)

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Research Program to Investigate the Fundamental Chemistry of Technetium

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Research Objective

Technetium (^{99}Tc, β emitter, half-life 2.1 x 10^5 years, spA= 1.7 x10^{-2} Ci/g) is one of the radionuclides of major concern because of regulatory considerations for radioactive waste disposal. The propensity of Tc as pertechnetate, TcO_4^-, to migrate in the geosphere necessitates its safe, long-term immobilization. Technetium is found in the nuclear waste storage tanks at the Hanford and at the Savannah River sites in highly alkaline environments along with multi-molar concentrations of nitrate, nitrite, and Na ions and lesser amounts of organic complexants, phosphate, sulfate chloride, fluoride, and carbonate. It has been assumed that technetium is present in the waste tanks as the pertechnetate ion but a recent study has suggested that at least in part, technetium is present in another form. There is a lack of information on Tc chemistry in oxidation states III-V with simple inorganic (OH^-, CO_3^{2-}, PO_4^{3-}, SiO_4^{4-}) and common organic ligands (EDTA, citrate, oxalate) under alkaline conditions. This is essential information needed for pretreatment schemes, processing, and the assessment of stability of Tc in waste form materials. Further complicating the Tc waste tank chemistry is the added effect of an intense radiation field originating from ^{137}Cs and ^{90}Sr. The interactions of the ionizing radiation with water, nitrate, nitrite, and other minor components create highly reactive species that can strongly perturb the oxidation-reduction conditions.

The stability of Tc in waste form materials is of paramount importance for long term storage concerns and the solid state chemical properties of many candidate Tc compounds are unknown. There have been few systematic studies of Tc stability in lower valent solids with the exception of TcO_2. Thus, it is not possible at present to assess the long term stability of many Tc compounds relevant to proposed waste form materials.

This experimental research program addresses the characterization of the chemistry of technetium pertinent to the waste tank environment and to various waste forms. The solution and solid state chemistry of this element will be studied in aqueous solutions as a function of pH with the various salts added such as nitrate and nitrite, and as a function of radiation dose. The second part of this program is a search for stable, lower valent Tc materials which may prove useful for waste storage.

Research Progress and Implications

This report summarizes the results after nine months of a three year project.

To determine the stability of reduced Tc species in solution we are testing the stability of a number of Tc^{4+} complexes with various complexing ligands as a function of pH. Samples of TcO_4^- in solution have been reduced with hydrazine and with H_3PO_2. These solutions have been treated with complexing ligands such as EDTA, citric acid, PO_4^{3-} and with varying concentrations of Cl^- with pH between 1 - 5. The above samples were examined by X-ray absorption spectroscopy (XAS) and preliminary data analysis indicates all samples contained Tc^{4+}. These samples are to serve as standards for subsequent work where the pH of the solutions will be changed to more basic values. These solutions will be subjected to gamma irradiation.

Earlier studies of Tc encapsulated in cements have shown that although the Tc was originally in the tetravalent state, it was slowly oxidized to TcO_4^- on a time scale of months to years. To determine if nitrate and/or nitrite play a role in the oxidation process, TcO_4^- was introduced in two synthetic salt

solutions and then encapsulated in cement. One salt solution contained both nitrate and nitrite as usual, but these anions were absent in the second salt solution. Two sets of Tc doped cements were prepared and in one set phosphate ion was added as a complexing agent for the reduced Tc species. XAS studies and preliminary data analysis show technetium present only as the Tc^{4+} in these cements.

Another facet of this investigation is the synthesis and characterization of reduced Tc and Re compounds. Although Re is not a good Tc surrogate in certain situations, it is useful in the development of synthetic routes. Initial investigations have centered around optimization of procedures for the generation of redox-pure oxohalides of technetium and rhenium in a variety of oxidation states. These complexes are suitable as precursors for complexation and precipitation studies. While known aqueous routes for the preparation of reduced forms of technetium can result in products of unreliable purity, non-aqueous preparations utilizing halogenating agents such as phosphorus pentachloride or chlorotrimethylsilane give very high yields of halogenated complexes such as $[MO_3Cl_2]^-$ (M = Tc, Re) and [*cis*-$ReO_2Cl_4]^-$. Further reaction time can give reduced products (such as in the direct isolation of $[TcOCl_4]^-$), while in other cases mild reducing agents can be employed to generate d^1- and d^2-oxohalide complexes. Structural determination of several members of this series (PPN[*cis*-ReO_2Cl_4], $PCl_4[ReOCl_5]$) have been undertaken to provide data for comparison with other oxohalide structures. Extension of these procedures to the generation of bromide and iodide analogs is possible through the use of trimethylsilylbromide or -iodide, respectively. The use of different halide precursors can yield different products from metathesis reactions.

Planned Activities

One of the major efforts of this program is to follow the reactions of TcO_4^- in alkaline aqueous solutions. This will be done with and without nitrate and/or nitrite present as a function of pH and of ionizing radiation dosage. We have considered using ^{60}Co as the method of irradiating the solutions. However, ^{60}Co has high energy gamma rays (~1.2 MeV) and the ionization in a small amount of solution will be limited. As an alternative we are exploring the use of ^{241}Am which has a 60 keV gamma ray that will be much more efficiently stopped by aqueous salt solutions. If one considers 1.5 g of ^{241}Am as a point source the amount of radiation from this source is about 20,000 R/hr. However, encapsulating this source will reduce the amount of radiation available. The fabrication of the containment vessel is underway as well as and the necessary permits to utilize a source of this magnitude are in process.

Tc solutions as described above will be prepared at more alkaline pH values. These solutions will be measured by XAS before and after gamma irradiation to characterize the Tc species. The original solutions used as standards will also be remeasured to determine the stability of the reduced species. All the Tc cements prepared in this project will be remeasured by XAS at three to six month intervals to determine if the reduced Tc species is being oxidized.

Based upon the premise that insolubility of precipitated products encapsulated in solid matrices may result in resistance to reoxidation and leaching of TcO_4^-, synthetic approaches are also being formulated for the generation of solubility-limited technetium complexes by either sol-gel condensation or precipitation routes. In particular, we have devised routes for the synthesis of alkoxide complexes (which may be useful in protonation reactions designed to generate precipitated products), and will examine the base-induced condensation of technetium and rhenium complexes of the formula $MO_3(OSiMe_3)$ to generate the dimeric heptoxides $M_2O_7L_2$ (L = Lewis base).

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

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Research Objective

Our goal is to develop a quantitative and mechanistic understanding of amorphous silica, SiO_2(am), dissolution kinetics in aqueous solutions. A knowledge of fundamental controls on the reactivity of simple Si—O bonded phases is the compositional baseline for understanding highly complex silica phases. In the Earth, silicate minerals comprise >70% of the crust and dominate virtually every subsurface system. More importantly for the objectives of this EMSP project, silicate minerals and materials are significant because compositionally complex silicate glasses will become the front line of defense in containing radioactive wastes in the nation's long term and interim storage strategies (Dove and Icenhower, 1997). To date, the behavior of SiO_2(am) is largely inferred from studies of the better known crystalline polymorphs (e.g. a-quartz). In the first step towards constructing a general model for amorphous silica reactivity in the complex fluid compositions of natural waters, we are determining the dissolution behavior as a function of temperature, solution pH and NaCl concentration. With these data we are determining relationships between SiO_2 glass structure and dissolution rates in aqueous solutions, as described below.

Research Progress and Implications

This report outlines our first year's progress and the resulting publications to date. In this experimental investigation, the dissolution kinetics of SiO_2(am) (fused and flame pyrolysis silica) were measured in solutions over the pH range of 4 to 10 containing 0.0 (deionized water, DIW) to 0.15 M NaCl at 40° to 275°C. Dissolution rates were determined in low temperature (40° to 80°C) and hydrothermal (120° to 275°C) reactor systems, using flow-through reactors that are broadly similar in design. Rate data collected from these two reactor designs are consistent with each other and yield the first comprehensive model of amorphous silica reactivity in deionized water and electrolyte solutions (Icenhower and Dove, 1998).

Measurements of rates show important similarities and differences between the corrosion behavior of SiO_2(am) and a-quartz. We find that the experimental energy of activation, $E_{a,xp}$, for the dissolution of SiO_2(am) is 75±5 kJ mol^{-1} in DIW. The introduction of up to 0.05 M NaCl yields similar $E_{a,xp}$ values of 80±5 kJ mol^{-1}. These values are Å10 kJ mol^{-1} higher than previous estimates of $E_{a,xp}$ for SiO_2(am) but are consistent with reported values of $E_{a,xp}$ for a-quartz. Dissolution rates measured at 200°C in DIW show that SiO_2(am) dissolves Å3 to 30X faster than a-quartz. A possible explanation for this difference is that SiO_2(am) has a fraction of Si-O-Si bonds (angles up to 180°) that have a greater ionic character, and are therefore more reactive than a-quartz constituents (mean angle of 152°) (Icenhower and Dove, in prep.). Measurements of SiO_2(am) dissolution rates versus NaCl concentrations at 200°C show that sodium enhances rates by a factor of Å10 to 30X compared to rates measured in DIW, which are less than rates for a-quartz under identical experimental conditions. In addition, we find that the dissolution rates of the two forms of SiO_2(am) (fused and flame pyrolysis silica) are similar within the experimental error of the early experiments. Results of this study suggest that the role of physical (structural) properties (e.g., Si-O-Si bonds) in governing reactivities of crystalline versus amorphous SiO_2 polymorphs is significant.

Planned Activities

Using these baseline findings, we will determine the rate-enhancing effects of cations, Li^{+}, K^{+}, Ca^{2+}, Mg^{2+}, and Ba^{2+}, that are often important rate-modifying constituents in natural subsurface waters. We will also determine the role of reaction affinity on the dissolution kinetics, and investigate the kinetics and mechanisms of Al^{3+} interactions with SiO_2(am) as a possible reaction inhibitor. Combining these studies with spectroscopic investigations of relationships between glass structure (as modified by water content) and measured reactivity, we will complete the project with a experimentally-based, comprehensive model of amorphous silica reactivity.

Other Access To Information

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Manuscripts in Advanced Preparation:

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Phase Chemistry of Tank Sludge Residual Components

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Kathryn L. Nagy, University of Colorado
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Research Objective

The proposed research will provide a scientific basis for predicting the long-term fate of radionuclides remaining with the sludge in decommissioned waste tanks. Nuclear activities in the United States and elsewhere produce substantial volumes of highly radioactive semi-liquid slurries that traditionally are stored in large underground tanks while final waste disposal strategies are established. Although most of this waste will eventually be reprocessed a contaminated structure will remain which must either be removed or decommissioned in place. To accrue the substantial savings associated with in-place disposal will require a performance assessment which, in turn, means predicting the leach behavior of the radionuclides associated with the residual sludges. The phase chemistry of these materials is poorly known so a credible source term cannot presently be formulated. Further, handling of actual radioactive sludges is exceedingly cumbersome and expensive. This proposal is directed at: (1) developing synthetic nonradioactive sludges that match wastes produced by the various fuel processing steps, (2) monitoring the changes in phase chemistry of these sludges as they age, and (3) relating the mobility of trace amounts of radionuclides (or surrogates) in the sludge to the phase changes in the aging wastes.

Research Progress and Implications

This report summarizes work carried out during the first year of a three year project. A prerequisite to performing a meaningful study was to learn in considerable detail about the chemistry of waste streams produced by fuel reprocessing. At Hanford this is not a simple task since over the last five decades four different reprocessing schemes were used: the early $BiPO_4$ separation for just Pu, the U recovery activity to further treat wastes left by the $BiPO_4$ activities, the REDOX process and most recently, the PUREX processes. Savannah River fuel reprocessing started later and only PUREX wastes were generated. It is the working premise of this proposal that most of the phase chemistry in the wastes was defined when the acidic process fluids were first neutralized prior to storage. The only notable exception being that some silicates obviously formed later under highly caustic conditions. Waste stream chemistries for each process have been established and surrogate sludges prepared. Aging of these different recipes have begun at 25º, 60º, and 90º C and the phase chemistry of the different mixes is being monitored.

One rather surprising development was the rapid formation of a cancrinite-group zeolite phase. This class of zeolites is unusual in that the structure contains a discrete anion, typically nitrate or carbonate in mineralogic studies, but the material may also sequester pertechnetate. Smaller amounts of a phosphate-containing zeolite also formed. A second unanticipated result was that goethite did not form as the dominant iron-containing phase in spite of the long heating some samples have experienced. Rather, X-ray diffraction suggests early formation of a mixture of ferrihydrite and layered material similar to reevesite ($Ni_6Fe_2CO_3(OH)_{16}.4H_2O$), with no subsequent tendency to form better crystallized phases. This disparity is ascribed to the high ionic strength and complex chemistry of the solutions from which the phases precipitated. We also detected a number of phases that would be expected based on bulk sludge chemistry such as boehmite and apatite, as well as a number of soluble salts (sodium sulfate phosphate, fluoro-phosphate, and, of course, sodium nitrate) that should disappear when the waste is leached.

As a reality check, the proposal also calls for comparisons with actual tank wastes. First, a substantial body of unpublished TEM data on Hanford tank sludges is to be synthesized (J. Liu). This report is in preparation and should be in draft form this Summer. TEM studies of the synthetic sludges are also underway and verify that: (1) the iron containing phase in the synthetic material is quite similar to that in actual sludges, and (2) that the zeolites noted previously may also occur in real sludges. Early attempts to duplicate $BiPO_4$ process wastes failed due to an incomplete understanding of the different waste streams. In particular, the sucrose appropriate to a PUREX waste was included in the $BiPO_4$ waste recipe. TEM studies revealed that this reduced the Bi to the metallic state. These experiments are being started again with the hope of forming the iron bismuth silicate hydroxide sometimes noted in early sludges.

Several mid-course corrections were needed once preliminary research results were available. In particular, a planned detailed study of aluminum phosphates was not initiated since it did not form in the sludge synthesis experiments, and present tank sluicing plans should dissolve any that already exists. Instead a detailed study of the evolution of apatite was initiated. Secondly, a recently completed tank closure demonstration at Savannah River, and conceptual designs for tank closure at Hanford, both imply that a reducing portland cement grout will probably be in intimate contact with the sludge. This could significantly impact the behavior of readily reduced radionuclides like Tc and U. Hot tests have been performed on a simple reducing grout composed of a dilute slurry of portland cement powder, ferrous ammonium sulfate and manganous chloride. As expected, in the first day the concentration of both Tc and U dropped by more than a factor of 50. But, exposure to air for an additional day caused the Tc to rebound. The behavior of Tc correlates well with the re-oxidation to pertechnetate. Indeed, repeating the same procedure with difficult to reduce perrhenate showed no dip in concentration, thus confirming that there is nothing in the system hydrous iron oxide - portland cement that serves as a sink for XO_4^- type anions. The behavior of U is more complex. After an initial precipitous drop additional U was slowly removed from solution to the point where it was no longer detectable (about 0.1 ppm U). Geochemical modeling using the code REACT suggests that portland cement alone should reduce U solubilities below the level noted after the first precipitous drop. Thus, it is likely that there is a kinetic barrier to the formation of solubility limiting U-phases. Other REACT

models dealing with radionuclide sorption on hydrous iron oxides in various environments are also underway.

Planned Activities

The primary focus of this proposal is on how the aging of sludge will impact radionuclide mobility. First, it was necessary to verify that representative materials could be produced outside of tanks. That has been completed. In the next six months bulk sludge syntheses experiments will be carried out in the presence of radioisotopes (or their surrogates). In the same time frame ageing studies will be initiated on simplified subsystems. The simplified systems to be addressed are: (1) hydrous iron oxides (and their hydrotalcite-like equivalents) in the presence of major amounts of Al and minor amounts of Ni and Cr (K.L. Nagy), (2) apatite - in particular the transition from hydroxyapatite to fluorapatite and its impact on coprecipitated radionuclides -or surrogates (P.v. Brady), and (3) the Fe-Bi-O,OH system (J.L. Krumhansl). The last year of the grant will focus on the desorption of radionuclides (or surrogates) from both the bulk sludges and the simplified subsystem materials.

Other Access To Information

Web page construction in progress: **http://www.sandia.gov/eesector/gs/gc/sludge.html**

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

Dr. M. Nafi Toksöz, Massachusetts Institute of Technology

Research Objective

This work is directed toward finding a way to estimate the properties of wastes in tanks on the Hanford Reservation. Data acquisition work (Turpening et al., 1995) has shown that acoustic measurements can be made inside a Hanford tank. Although that data was collected in a cross-well geometry, other data acquisition methods are now of interest. In particular, it would be very useful if an estimate of the properties of the wastes could be made by lowering a single string of hydrophones into the one liquid observation well (LOW) that exists in every tank while activating a seismic source on the surface outside the tank.

Such an endeavor requires an understanding of the normal modes of oscillation of a Hanford tank when it contains various layers of wastes. The objective of this study to gain that understanding.

With advent of the cone penetrometer it is now possible to conduct acoustic cross-well measurements in a Hanford tank even though each tank has only one LOW. This in turn makes the study of normal modes even more important since these modes of oscillation constitute a major portion (along with tube waves) of the background noise in any cross-well data set. Knowing where the normal modes exist in the frequency domain, for example, will allow one to plan a data acquisition program that might avoid the especially strong modes.

Research Progress and Implications

The initial period of this study has focused on tanks containing non-rigid wastes, i.e. where only acoustic waves propagate in the waste materials. We have approached the problem both theoretically and by means of laboratory-sized scale models. The theoretical work has shown, and the lab

measurements have confirmed what was expected, that the spatial complexity of the modes increases as frequency increases. The low frequency modes show a simple vertical distribution of pressure while the higher frequency modes (Figure 1) show a more complex distribution of pressure in the tank. In all of this work we assume that the tank is rigid

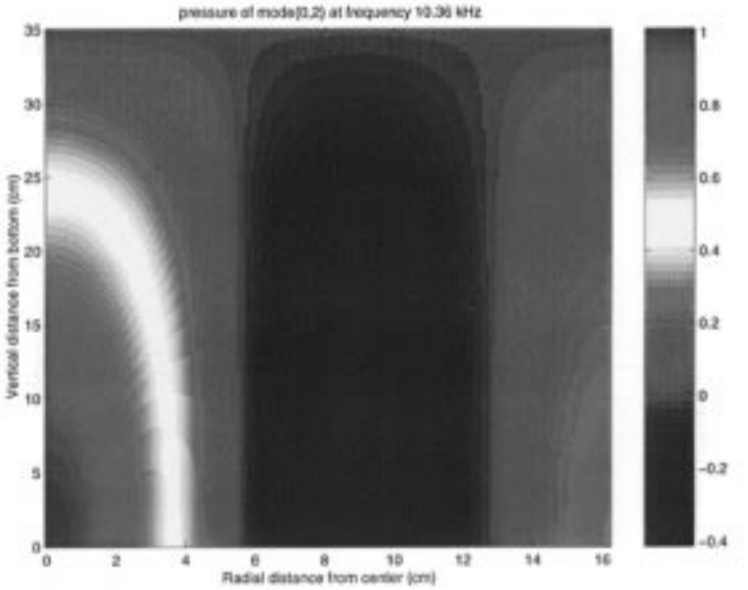

Figure 1. Display of the distribution of pressure in a vertical plane for one half of a tank. The source is on the center line of the tank half-way between the bottom and the surface of the liquid. This is a mode that would occur at approximately 138 Hz in a full-size Hanford tank. Reference: **Turpening, R., Z. Zhu, C. Caravana, J. Matarese, W. Turpening, 1995,** ***Acoustic imaging of underground storage tank wastes-A feasibility study*****, Westinghouse Hanford Co., Richland, WA.**

The implications of the work to date are twofold. First, the modes are rich in information, especially when the vertical array of hydrophones is not on the center line of the tank. Fortunately, that will be the case with many of the Hanford tanks. Second, it is clear that any future cross-well measurements in a tank should be made at high frequencies to avoid the strong fundamental modes. Again, this would be the normal action taken by any data acquisition specialist.

Planned Activities

Currently, we are treating the case of two liquid layers of waste, both theoretically and in the lab. In addition, we are including the standing waves in the sides of the steel tank. In the third year we will conduct a data acquisition program inside a Hanford tank to collect normal mode data. This will be performed in much the same manner as our successful work performed in 1994.

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

Dr. Philip E. Zapp, Savannah River Technology Center

Dr. John Van Zee, University of South Carolina

Research Objective

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

Research Progress and Implications

This report summarizes progress after approximately six months of effort in this three-year EMSP project. Initial experimental and theoretical work has focused on the electrochemical behavior of carbon steel in simplified non-radioactive solutions that simulate complex dilute radioactive waste solutions. These solutions contain corrosion-inducing species such as nitrate and chloride and the corrosion-inhibiting nitrite at moderately alkaline pHs. The electrochemical behavior of interest here is that of the open-circuit potential of the steel specimen at equilibrium in the experimental electrolyte and the measures of the steel's passivity and passivity breakdown.

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

Electrochemical Studies

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

Initial experiments demonstrate significant differences in the steel's behavior in nitrate versus chloride solutions. Chloride is the classic initiating ion of pitting corrosion. With increasing chloride concentration in the range 0.01 to 0.3 M, the breakdown potential decreases from a value above the transpassive transition (~ 750 mV SCE) to a value below the open-circuit potential (open-circuit potentials range from -500 to -100 mV SCE). Chloride-induced breakdown is mitigated by nitrite;

nitrite drives the breakdown potential higher. Nitrate has been shown to induce pits in carbon steel, and such pitting can also be mitigated by nitrite. In fact the action of nitrite is empirically the same for nitrate and chloride. However, in the present experiments increasing nitrate concentrations do not result in the observation of a breakdown potential. CPP scans in solutions with a nitrate concentration of as high as 2.2 M continue to show a transpassive transition at about 750 mV SCE. The corrosivity of nitrate toward carbon steel is revealed in an increase in the passive current density.

Spectroscopic Studies

In addition to the potentiodynamic polarization scans, spectroscopic studies have been started. The goal of these studies is to investigate the oxide film and its response to changes in the concentration of corrosive and protective species with in-situ vibrational spectroscopy. A specially designed cell has been constructed to allow for combined Electrochemical Impedance Spectroscopy and FTIR or FT Raman measurements. These EIS/FTIR and EIS/FT Raman cells will be used to determine if surface enhanced signals can be observed. Raman/EIS cells are being tested using a number of optical configurations. One of these designs will be used to test the cell optics and Raman sensitivities and it will incorporate two glass plates. A thin metallic film will be deposited on the inner surface of one plate. The space between the plates will contain the test solution. Counter and reference electrodes have been installed. The cell can then be positioned in the Raman spectrometer in two orientations: (1) the exciting beam passes through the unmetallized plate and solution before striking the metal film; and (2) the beam enters through the back of the metallized plate and strikes the film from the rear. The evanescent Raman from this orientation will minimize optical sampling of the solution.

Analysis and Modeling

The analysis of the passivation/activation phenomena will be aided by a fundamental understanding of the solution chemistry and the adsorption characteristics of chloride, nitrate, and nitrite as a function of temperature and ionic strength. Studies of the interaction of nitrate and nitrite may involve the redox reactions shown by reactions 1-5 below. As a first step in the analysis of the solution effects, the effect of ionic strength on the equilibrium and solubility products for the Pourbaix diagram has been calculated using equation 6. Here the dilute solution equilibrium constant, Keq and the actual equilibrium constant Qeq are related to the ionic strength, I, the molality of the dominant species. We believe that the effect of temperature will be reflected in the equilibrium solubility products, the hydrolysis reactions, and the exchange current densities for film breakdown.

U(V)

$1/2NO_3^- + 1/2H_2O + e^-$ go to $1/2NO_2^- + OH-$ 0.011 (1)

$1/6NO_2^- + 5/6H_2O + e^-$ go to $1/6NH_3 + 7/6OH^-$ -0.165 (2)

$1/3NO_2^- + 2/3H_2O + e^-$ go to $1/6N_2 + 4/3OH-$ 0.406 (3)

$1/2NO_2^- + 3/4H_2O + e^-$ go to $1/4N_2O + 3/2OH-$ 0.151 (4)

$H_2O + e^-$ go to $1/2H_2 + OH^-$ -0.828 (5)

logQ = logK a*rootI/(1+rootI) +b*m (6)

Planned Activities

Activity Completion

1. Perform potentiodynamic and potentiostatic scans to evaluate the differences in the chloride and nitrate effects on the breakdown potential and passivecurrent density 12/98.
2. Spectroscopic studies to design & fabricate EIS/FTIR and EIS/FT Raman cells 9/98.
3. Perform measurements to check for surface enhancement and study the effect of the exciting beam passing through the solution before striking the metal film and the effect of the exciting beam passing through the back of the metallized plate and striking the film from the rear 9/99.
4. Mathematical model of pitting phenomena 9/00.

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

Dr. Thomas E. Mallouk, Pennsylvania State University

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

Research Objective

The objective of the project is to develop and characterize supported reducing agents, and solid waste forms derived from them, which will be effective in the removal of transition metal ions, chlorinated organic molecules, and technetium from aqueous mixed wastes. This work follows the discovery that a nanoscale form of zero-valent iron, dispersed on high surface area supports, reduces metal ions (chromium, mercury, and lead) and rhenium (as a surrogate for technetium) to insoluble forms much faster than does unsupported iron.

The scientific goals of the project are to better understand the mechanism of the reduction process, to develop supports that are compatible with a variety of mixed waste compositions, and to develop surface modifiers for the supported iron aggregates that will optimize their selectivity for the contaminants of interest. The support composition is of particular interest in the case of technetium (Tc) separation and stabilization in the Hanford tank wastes. While it is expected that pertechnetate will be reduced insoluble TcO_2, the support material must be compatible with the vitrification process used in the final waste disposition. The surface modifications are also a focal point for Hanford applications because of the complex and variable makeup of the tank wastes.

Research Progress and Implications

This report summarizes progress in the first 8 months of a 3-year collaborative project involving Penn State and Pacific Northwest National Laboratory (PNNL). Aggregates of 10-30 nm diameter iron particles have been prepared by reduction of iron salts onto various supports, including silica, Polyflo resin (a non-porous, high surface area polymer supplied by Puresyn, Inc., Malvern, PA), monoclinic ZrO_2, and SnO_2. The kinetics of reduction of aqueous 0.5 mM CrO_3, $PbCl_2$, $Hg(OAc)_2$, $CdSO_4$, and NH_4ReO_4 were studied with these materials ("Ferragels"), and compared to those of unsupported iron. The most easily reduced metals (Cr, Pb, Hg) are removed to levels below the detection limits of atomic absorption spectroscopy, typically 2-20 ppb, and the rates of these reactions are substantially faster than with activated, unsupported iron. A colorimetric test has been developed for studying the corrosion reaction of the particles, and was used to evaluate different monolayer-forming molecules as corrosion inhibitors. These studies are intended to lay the groundwork for design of contaminant-selective monolayer coatings.

The mechanism of metal ion reduction appears to be complex, involving rapid surface adsorption followed by a slower outer-sphere electron transfer step. The reduction processes for Cr, Hg, Pb, and Cr species were first order with respect to amount of supported iron. The rate constants (normalized per gram of supported iron on Polyflo) were 8.9×10^{-2} (Hg), 3.5×10^{-2} (Pb), 1.2×10^{-3} (Cd), and 6.1×10^{-3} s^{-1} (Cr). The rate increases monotonically with increasing E_0, the standard potential for the metal ion, except in the case of Cr, where the potential for one-electron reduction to Cr(V) differs considerably from E_0 for the three-electron $Cr^{6+/3+}$ couple. This trend suggests that outer-sphere electron transfer is the rate-determining step in the reaction. For Cr, which was studied in detail, the reaction is second order in [Cr], suggesting that the kinetics are further complicated by aggregation of aquo ions. XPS confirms that Cr(VI) is reduced to trivalent insoluble forms, most probably $Cr(OH)_3$ or Cr_2O_3. This mechanistic study will be completed in the near term. In this connection, Pb(II)

should be a simpler test system than either Cr(VI) or Hg(II), because it is monomeric and has only one oxidation state in solution.

An interesting variation in reduction rates was found with different high surface area supports. Using Polyflo, a proprietary, non-porous, high-surface-area resin, the rate of Cr(VI) reduction was six times greater than with chromatographic silica under identical conditions. Nitrogen BET analysis shows that iron-on-Polyflo Ferragel (190-200 mg Fe / g) has a surface area of 38 m^2/g with little adsorption/desorption hysteresis, compared to iron-on-silica (243 m^2/g). Most of the iron in silica Ferragel is deposited in relatively inaccessible mesopores, whereas the non-porous Polyflo resin effectively presents all of the iron nanoparticles to the solution.

Surface modifying layers are being studied as a way of improving the selectivity of the reduction process. One problem with the Hanford tank wastes is that they contain other oxidizing agents, including nitrite (NO_2^-), as well as various anions (hydroxide, carbonate, nitrate, etc.) at high concentration. Nitrite efficiently oxidizes zero-valent iron in the absence of surface modifiers. Thus, we are looking for a surface modifier that selects TcO_4^- and possibly soluble complexes of Tc(IV) from a solution containing anions of higher charge density. Hydrophobic quaternary ammonium ions are selective for hydrophobic anions, but do not adsorb to the iron surface, and so a method of attachment must be found. Towards this end, tetrahexadecylammonium bromide, tridodecylmethylammonium iodide, sodium hexadecylsulfonate, octylphosphonic acid, and phenylphosphonic acid were tested as corrosion inhibitors for iron-on-Polyflo Ferragel. The surfactants were adsorbed from alcohol, then tested in aqueous pH 5.5 solutions of 1,10-phenanthroline (5g/L) These studies show that simple quaternary ammonium salts, alkyl sulfonates, and alkyl/arylphosphonates do not inhibit acid corrosion of iron significantly. Other surfactants containing more aggressive head groups (thiolate, dithiocarbamate, carboxylate, hydroxamate) and polymeric surface modifiers are now being tested.

Planned Activities

Work will continue on the search for an appropriate surface modifier — with a particular emphasis on the Hanford nitrite vs. pertechnetate problem. Compounds to be tested include molecules known to form self-assembled monolayers (SAMs), and polymers containing the same surface-active groups. We will measure equilibrium constants for adsorption of thiolates, dithiocarbamates, carboxylates, and hydroxamates on iron nanoparticles. Polymerized versions of any reversibly-binding monomer that shows significant corrosion resistance should provide a more stable, non-desorbing protective layer. Once the appropriate head group and surfactant structure (monomer or polymer) is selected, compounds containing quaternary ammonium groups will be synthesized and tested for selective binding of pertechnetate. Similar “tail group” strategies will be applied to selecting for transition metal cations (using ligating groups) and for hydrophobic organic waste components, such as Tc(IV)EDTA and chlorocarbons (using nonpolar tail groups).

As work progresses with surface modification, iron nanoparticles on different support materials will be tested on Tc-containing samples at PNNL. These support materials will include tin oxide, zinc oxide, Polyflo resin, and high surface area cubic zirconia prepared hydrothermally at PNNL. In anticipation of receiving candidate absorbent materials from Penn State for Tc K_d testing, PNNL has made preparations for having Tc isotopes and liquid waste simulants ready. Scoping experiments have been performed on preparing high surface area zirconia-based powders using PNNL’s hydrothermal powder production technology, and on pelletizing them into potential supports for iron nanoparticles. PNNL will conduct K_d testing for Tc, and will test the support materials for stability under simulated tank waste conditions.

Addition of another researcher at Penn State in Fall, 1998 allows expansion of the project to aqueous wastes containing halogenated hydrocarbons. Zero valent iron is a demonstrated remediant for these wastes, and the focus of our work with Ferragel will be to to control selectivity using appropriate SAMs. Initially, perchlorethylene will be tested as a model contaminant, because the product distribution can provide information on whether hydrolytic dehalogenation or reductive hydrogenation is the operative reaction pathway with supported, SAM-derivatized iron.

Work at PNNL will build on successful reduction of Tc waste simulants by studying the vitrification and subsequent stability of Ferragel supports, as well as actual spent, Tc-containing, Ferragel. If accessible, testing will progress to actual tank waste. Work on metal remediation with iron-on-Polyflo Ferragel will progress to proof-of-concept studies on actual heavy metal wastes — most likely Pb — at site(s) in Pennsylvania.

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

Dr. Norman C. Schroeder, Los Alamos National Laboratory

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

Research Objective

The ultimate goal of this proposal is to separate technetium from Hanford tank waste. Our recent work has shown that a large portion of the technetium is not pertechnetate (TcO_4^-) and is not easily oxidized. This has serious repercussions for technetium partitioning schemes because they are designed to separate this chemical form. Rational attempts to oxidize these species to TcO_4^- for processing or to separate the non-pertechnetate species themselves would be facilitated by knowing the identity of these complexes and understanding their fundamental chemistry. Tank characterization work has not yet identified any of the non-pertechnetate species. However, based on the types of ligands available and the redox conditions in the tank, a reasonable speculation can be made about the types of species that may be present. Thus, this proposal will synthesize and characterize the relevant model complexes of Tc(III), Tc(IV), and Tc(V) that may have formed under tank waste conditions. Once synthesized, these complexes will be used as standards for developing and characterizing the non-pertechnetate species in actual waste using instrumental techniques such as capillary electrophoresis electrospray mass spectrometry (CE-MS), x-ray absorbance spectroscopy (EXAFS and XANES), and multi-nuclear NMR (including ^{99}Tc NMR). We will study the redox chemistry of the technetium complexes so that more efficient and selective oxidative methods can be used to bring these species to TcO_4^- for processing purposes. We will also study their ligand substitution chemistry which could be used to develop separation methods for non-pertechnetate species. Understanding the fundamental chemistry of these technetium complexes will enable technetium to be efficiently removed from the Hanford tank waste and help DOE to fulfill its remediation mission.

Research Progress and Implications

This report summarizes the first 8 months of a 3-year project. Our efforts have so far been directed at the synthesis and characterization of technetium and rhenium complexes. The initial development work has been made using rhenium, the chemical analogue of technetium, which also forms dinuclear m-oxo complexes. This is allowing more rapid development of this program because the concerns of working with radioactivity is eliminated. The techniques developed with the rhenium analogues are then transferred to the technetium work. Complexes synthesized to date have been $[(HEDTA)Re(m\text{-}O)2Re(HEDTA)]_2^-$, $[(NTA)Re(m\text{-}O)2Re(NTA)]_2^-$, $[(tetn)Re(m\text{-}O)2Re(tetn)]_4^+$ (tetn = triethylenetetraamine), and $[(C_2O_4)2Re(m\text{-}O)2Re(C_2O_4)_2]_2^-$. These complexes have been synthesized at pH 4 using ReOCl52- or ReCl62- as starting materials. The complexes are very water soluble and difficult to isolate. We have studied the reactivity of these complexes in sodium hydroxide solutions,

conditions similar to the Hanford tank waste. Rapid scanning UV-VIS experiments suggest that the complexes oxidize quickly to a Re(IV)/Re(V) complex and slowly to a Re(V)/Re(V) species and eventually to ReO_4^-. The oxidation is promoted by higher base concentrations and the extent of exposure to air. The order of reactivity is oxalate > NTA > EDTA. The $[(HEDTA)Tc(m\text{-}O)2Tc(HEDTA)]_2^-$ complex has been synthesized from pertechnetate at pH 4. We have measured the distribution coefficient (Kd) of this complex between Reillex-HPQ anion exchange resin and solutions of the complex that range in pH from 1-14. In the presence of nitrate the complex fails to sorb on the resin at any pH. Without nitrate present the complex does sorb. At pH <2 the sorption is low because the complex is neutral. Above pH 2 sorption does occur as the complex deprotonates to form initially a 2-, then 3- and 4- anionic species. The maximum sorption, Kd values > 300 mL/g, occur at pHs between 5-9. Above pH 10 the Kd values decrease as the complex begins to oxidize. As with the rhenium complexes, we speculate that a Tc(V)/Tc(V) species is forming which then oxidizes to pertechnetate. However, this is occurring at a slower rate compared to the rhenium complexes.

This project is collaborating on the purchase and assembly of a capillary electrophoresis mass spectrometry (CE-MS) instrument. The HP engine mass spectrometer has been delivered and is currently being assembled. The capillary electrophoresis section of the instrument will be interfaced with the MS through an Analytica electrospray source. The estimated sensitivity of the CE/MS unit is at the attomole to picomole level which would make it possible to detect < 10^{-8} M of a non-pertechnetate species in a mL of waste. We are using the rhenium and technetium complexes that we synthesize as standards to help develop capillary electrophoresis mass spectrometry (CE-MS) as a method for characterizing the technetium species in actual wastes. Capillary electrophoresis has been shown to provide separation efficiencies above 106 theoretical plates, allowing separation of complex mixtures before introduction into the mass spectrometer for analysis. Total sample usage is very small (~1 nL), making this type of instrument attractive for use with radioactive samples.

Our collaborator, Dave Blanchard, at PNNL has studied the XAS spectra of $[TcO_2(en)]+$ (en = ethylenediamine) and NH_4TcO_4 under acidic conditions and compared the spectra to the non-pertechnetate Tc species present in tank waste and to the $[(HEDTA)Tc(m\text{-}O)2Tc(HEDTA)]_2$-complex prepared by the LANL group. The data are currently being analyzed. A paper is being prepared for publication with the results of an X-ray Absorption Near Edge Spectroscopy (XANES) analysis of the Tc in samples of waste from Hanford tanks AN-107, AW 101, SY-101, and SY-103. Both pertechnetate and non-pertechnetate Tc species are present in all untreated samples. Pertechnetate is almost completely removed by contacting the waste samples with Reillex-HPQ anion exchanger. The highest concentration of the non-pertechnetate was found in waste with the highest organic complexant concentration, suggesting the presence of a Tc species complexed or bound to complexants or complexant fragments. The XANES of the Tc in these treated samples (which varies from 20% to 80%, depending on the tank) is consistent with a Tc(IV) species bound to complexants or complexant fragments through oxygen linkages. Spectra of one of the wastes (SY-103) before and after aging for approximately 4 months shows an increase in the fraction of pertechnetate present, indicating oxidation of the non-pertechnetate to pertechnetate.

Planned Activities

We will finish synthesizing the first series of polyaminopolycarboxylate and aminopolycarboxylate rhenium complexes that will give us complexes containing donor atoms sets ranging from four oxygens through four nitrogens. We will make the corresponding technetium complexes. All complexes will be examined for their reactivity in basic solution. The complexes will be used for the XAS, XANES, and CE/MS work. This work will occur through the summer and into the start of the nest fiscal year.

Other Access To Information

N.C. Schroeder, S.D. Radzinski, K.R. Ashley, A.P. Truong, and P.A. Szczepaniak, “Technetium Oxidation State Adjustment for Hanford Waste Processing,” accepted for publication in Science and Technology for Disposal of Radioactive Tank Waste, N.J. Lombardo and W.W. Schulz, eds., Plenum Publishing Corporation, New York, NY, (1997)

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

Dr. Stephen F. Agnew, Los Alamos National Laboratory

Clifford T. Johnston, Purdue University

Research Objective

The concentrated caustic waste slurries stored in waste tanks at Hanford and Savannah River have large amounts of aluminate along with nitrate, nitrite, hydroxide, carbonate, and phosphate-all species are present both in solution and as solids. The dominant cation is sodium with few percent potassium and other species. These slurries have sodium concentrations on the order of 10-15 mol/L and therefore very high ionic strengths and low water activities. These slurries have been the source of many safety problems at Hanford and Savannah River Sites and the slurry rheologies, gelling points, and gas retention properties are largely responsible for those safety issues.

Even though both Hanford and Savannah River have produced large volumes of these slurry concentrates, the microstructural properties that are important for understanding slurry behavior are not well understood. For example, aluminate solid formation has been associated with Hanford concentrates, but is not observed at Savannah River. Another example is that although hydrogen gas retention in slurries is a prevailing safety issue at Hanford, it is only a relatively minor issue in SRS tanks.

Research Progress and Implications

This project is in the second year of a three year effort. A very important property of these slurry concentrates is water activity. Water activity is manifest as its vapor pressure in equilibrium with each slurry. We have found that aluminate in both solution and solid have dramatic effects on water activity. For example, the monosodium aluminate solid, MSA, is only stable at around 22% relative humidity at 20° C. If one attempts to store MSA at humidities greater than this equilibrium, the solid rapidly deliquesces or absorbs water until it redissolves.

This behavior of MSA explains why in can never be stored in waste tanks at Savannah River. The seasonal average relative humidity at Savannah River is on the order of 40%, which therefore precludes long term MSA storage.

With increasing aluminate concentration, the aluminate dimerizes thereby releasing water. Concentrating aluminate solutions normally produces increasing amounts of dimer. However, the dimer can only exist in particular ranges of water activity. If the water vapor pressure increases, the solution readily absorbs water as the dimer shifts to the monomer. We have found that the water activity for aluminate solutions can be predicted based on the extent of dimerization as well as excess hydroxide. Thus, a particular aluminate concentration is only stable up to sum limiting water vapor.

Precipitation of monsodium aluminate from solution releases water as

$$Al(OH)_4^- \text{ (solution)} \rightarrow 1/2\ Al_2O_3(OH)_2^{2-} \text{(solid)} + 0.75\ H_2O \text{ (free)} + 0.75\ H_2O \text{ (hydration)}$$

The solution aluminate, then, actually ties up much more water than does the MSA solid. The waters of hydration in MSA are strongly hydrogen-bonded in channels within its lattice as shown in Fig. 1.

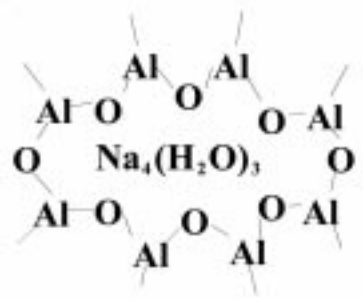

Fig. 1. View down the unusual ion channel of monosodium aluminate (MSA), tetragonal, $P\bar{4}2_1m$ $Na[AlO_{1.5}(OH)]\cdot 0.75H_2O$.

These waters of hydration are much more strongly perturbed than, for example, waters of hydration in clay minerals. The "free" water is characterized by HOH stretch doublet at 3250 and 3440 cm^{-1} and an HOH deformation at 1660 cm^{-1}. There is a "bound" form of water with a very broad HOH stretch at 3040 cm^{-1} and an HOH deformation shifted to 1590 cm^{-1}. This highly perturbed water is evidently associated with a hydrogen-bonded solution and solid form since these features persist in MSA solid. We have further explored the effect of nitrate, nitrite, and carbonate ions on the solution and slurry properties. Sodium nitrate and nitrite seem to act primarily as diluents when combined with aluminate. The aluminate dimer equilibrium shifts in a manner similar to that of simply diluting with increasing water concentration.

Carbonate ion, on the other hand, has a much more pronounced affect on the solution aluminate equilibrium. The source of carbonate in concentrated wastes has been primarily that absorbed from the atmosphere by reaction with the caustic waste. Aluminocarbonate solids are well known, but the nature of the aluminocarbonate solution interaction in caustic solution is not known. The presence of carbonate somehow destabilizes the aluminate dimer causing a shift back to monomer for reasons that we still do not entirely understand. However, infrared spectroscopy suggests that the carbonate is weakly monodentate in these solutions, showing a doublet absorption at 1380 and 1440 cm^{-1}. This suggests that there is an aluminocarbonate species formed in these solutions.

Planned Activities

We plan to explore the nature of the aluminate in the presence of carbonate and obtain infrared absorption of solutions and solids, and better correlate the water activity with its Raman and infrared features. In particular, we will correlate the two types of water present in these mixtures with the slurry water vapor pressure. Finally, we hope to explore the interaction of soluble organic complexants with aluminate in solution. We feel that there will be an interaction similar to that we observe for carbonate.

Other Access To Information

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"Raman Scattering, Infrared Absorption, and Relative Humidity of Mono- and Trisodium Aluminate," paper presented at I&EC Division symposium on Radioactive and Hazardous Waste Forms, ACS National Meeting in Dallas in March 1998.

Mixed Waste

Architectural Design Criteria for F-Block Metal Ion Sequestering Agents

Dr. Benjamin P. Hay, Pacific Northwest National Laboratory

Dr. David A. Dixon, Pacific Northwest National Laboratory
Prof. D. Max Roundhill, Texas Tech University
Prof. Robin D. Rogers, The University of Alabama
Prof. Robert T. Paine, University of New Mexico
Prof. Kenneth N. Raymond, University of California at Berkeley

Research Objective

The objective of this project is to provide a means to optimize ligand architecture for f-block metal recognition. Our strategy builds on an innovative and successful molecular modeling approach in developing polyether ligand design criteria for the alkali and alkaline earth cations. The hypothesis underlying this proposal is that differences in metal ion binding with multidentate ligands bearing the same number and type of donor groups are primarily attributable to intramolecular steric factors. We propose quantifying these steric factors through the application of molecular mechanics models.

The research involves close integration of theoretical and experimental chemistry. The experimental work entails synthesizing novel ligands and experimentally determining structures and binding constants for metal ion complexation by series of ligands in which architecture is systematically varied. The theoretical work entails using electronic structure calculations to parameterize a molecular mechanics force field for a range of metal ions and ligand types. The resulting molecular mechanics force field will be used to predict low energy structures for unidentate, bidentate, and multidentate ligands and their metal complexes through conformational searches. Results will be analyzed to assess the relative importance of several steric factors including optimal M-L length, optimal geometry at the metal center, optimal geometry at the donor atoms (complementarity), and conformation prior to binding (preorganization). An accurate set of criteria for the design of ligand architecture will be obtained from these results. These criteria will enable researchers to target ligand structures for synthesis and thereby dramatically reduce the time and cost associated with metal-specific ligand development.

Research Progress and Implications

Substantial progress has occurred in the first eighteen months of this project. Our research to date has focused on the amide functional group. We have synthesized twenty multidentate amide ligands ranging from simple diamides such as tetraalkylmalonamides to more complicated calixarene derivatives. The coordination chemistry of these ligands with actinides and lanthanides is under investigation. Solution phase stoichiometries for metal diamide complexes have been determined by infrared spectrophotometric titrations and by solvent extraction results. In the majority of cases the same stoichiometries were observed in the solid state using thermal gravimetric analysis and single crystal X-ray diffraction. Fourteen novel structures have been obtained. These include the first crystal structures of lanthanide succinamide complexes, revealing a rich and varied coordination chemistry for this diamide.

A variety of methods for the determination of metal amide binding constants have been investigated. Calorimetry has yielded the first binding constants for diamides with any metal ion. Binding constants for 1:1 ligand:metal complexes have been measured for six diamides with trivalent europium, quantifying a significant effect of ligand architecture on complex stability. Similar effects were obtained with a solvent extraction method, confirming the calorimetry results. Solvent extraction studies also

have yielded the first example in which calixarene conformation is observed to effect the extraction of the uranyl ion.

An extended MM3 model has been developed for metal amide complexes. Force field development has required the refinement of existing amide parameters and the generation of new parameters for the metal-amide interactions. This has been accomplished using both electronic structure calculations and experimental data (crystal structures). We have found that each metal requires a different set of parameters. A unique feature of the parameterization is that the metal-dependent parameters are correlated with metal ion properties. Thus, the model can be applied to any metal ion in the Periodic Table. The performance of the model has been validated by comparison of calculated and observed structural features. A total of 56 crystal structures were used in this comparison including amide complexes with alkaline earth, transition metals, lanthanides, and actinides. A marked difference was observed in amide orientation with transition metals when compared to the f-block metals. This observation provides criteria to design amide ligand architecture with optimal complementarity for actinides.

Planned Activities

Our research program will focus on the amide function group for the rest of this year and into FY99. Characterization of actinide diamide complexes is in progress. Additional succinamide derivatives will be prepared to evaluate the effect of the degree of bridge alkylation. The structure-function data sets in diamides will be expanded by the continued application of calorimetry and solvent extraction methods to measure additional binding constants. Additional calixarene amides will be prepared and characterized.

Conformational analyses of malonamide and succinamide derivatives is in progress. All geometries and relative energies obtained with the model will be verified by geometry optimizations and frequency calculations obtained from electronic structure calculations. Ligand strain energies will be evaluated for all the diamides for which binding affinities have been measured. Comparison of binding affinity with ligand strain will indicate to what extent ligand steric demands influence complex stability. The results of this study will be used evaluate the extent of improvement that can be obtained by the structural modification of diamides.

Other Access To Information

Further details on this research are available in progress reports PNNL-11589 and PNNL-11899. Results of this research have been presented in fifteen talks at scientific conferences and are documented in thirteen publications:

(1) Falana, O.M.; Koch, H.R.; Roundhill, D.M.; Lumetta, G.J.; Hay, B.P. “Synthesis and Extraction Studies of 1,2- and 1,3-Disubstituted Butylcalix[4]Arene Amides with Oxyions: Geometric and Conformational Effects.” J. Chem. Soc. Chem. Commun. 1998, 503-504.

(2) Hay, B.P.; Clement, O. “Metal Complexes” in Encyclopedia of Computational Chemistry, P. von Rague Schleyer, Editor-in-Chief, John Wiley and Sons, London, in press.

(3) Clement, O.; Rapko, B.M.; Hay, B.P. “Structural Aspects of Metal-Amide Complexes.” Coord. Chem. Rev., in press.

(4) Rao, L.; Xia, Y.; Rapko, B.M.; Martin, P.F. “Synergistic Extraction of Eu(III) and Am(III) by Thenoyltrifluoroacetone and Neutral Donor Extractants: Octyl(Phenyl)-N,N-Diisobuty-lcarbonyl-methylphosphine Oxide and 2,6-Bis(Diphenylphosphino)methyl Pyridine N,P,P Trioxide.” Solv. Extr. Ion. Exch., in press.

(5) Yordanov, A.; Roundhill, D. M. “Solution Extraction of Transition and Post-Heavy and Precious Metals by Chelate and Macrocyclic Ligands.” Coord. Chem. Rev., in press.

(6) Lumetta, G.J.; Rapko, B.M.; McNamara, B.K. “Using Excel” to Analyze Liquid-Liquid Extraction Equilibria.:” J. Chem. Ed., submitted.

(7) Wolf, N.J.; Georgiev, E.M.; Yordanov, A.T.; Whittlesey, B.L.; Koch, H.F.; Roundhill, D.M. “Synthesis of Lower Rim Amine and Carbamoyl Substituted Calixarenes as Transfer Agents for Oxyions between an Aqueous and a Chloroform Phase.”Inorg. Chem., submitted.

(8) Yordanov, A.T.; Wolf, N.J.; Georgiev, E.M.; Koch, H.F.; Falana, O.M.; Roundhill, D.M. “Derivatized Calix[4]arenes as Selective Phase Transfer Extractants for Heavy Metal and Oxyion Salts.” Comm. Inorg. Chem., submitted.

(9) McNamara, B.K.; Lumetta, G.J.; Hay, B.P.; Rapko, B.M.; and Rogers, R.D. “Coordination Chemistry of Lanthanide Nitrates with N,N,N,N-Tetramethylsuccinamide.” Inorg. Chem., submitted.

(10) Hay,B.P.; Clement, O.; Sandrone, G.; Dixon, D.A. "A MM3(96) Force Field for Metal-Amide Complexes." Inorg. Chem., submitted.
(11) Sandrone, G.; Dixon, D.A.; Hay, B.P. "C(sp2)-C(sp3) Rotational Barriers in Simple Amides: H_2N-C(=O)-R, R = Methyl, Ethyl, i-Propyl, t-Butyl." J. Phys. Chem. submitted.
(12) Rao, L.; Zanonato, P.; Di Bernardo, P. "Studies of Europium(III) Complexation with Tetramethylmalonamide and Tetramethylsuccinamide in Organic Solvents by Calorimetry and Optical Spectroscopy." Inorg. Chim. Acta, manuscript in preparation.
(13) Dixon, D.A.; Sandrone, G.; Hay, B.P. "Computational Studies of Cation Binding to Amides. I. Proton Binding Affinity." J. Phys. Chem., manuscript in preparation.

Rational Design of Metal Ion Sequestering Agents

Dr. Kenneth N. Raymond, Lawrence Berkeley National Laboratory

Research Objective

This project addresses fundamental issues and requirements in developing hazardous metal ion separation technologies needed in the treatment and disposal of radioactive and chemical toxic waste. It encompasses the synthesis of new agents, followed by their characterization and evaluation, with the aim to optimize their metal ion sequestering properties for use in applied technologies. This research is focused on the following key areas: (i) basic design and synthesis of new metal ion specific sequestering ligands; (ii) structural and thermodynamic investigations of these ligands and their complexes formed with the targeted metal ions; and (iii) development of sequestering agents and their incorporation into systems designed to be prototypes of inexpensive and highly effective materials for hazardous metal ion decontamination. Basic studies of the sequestration of relevant toxic metals are required in order to develop processes that will treat effluents sufficiently well to allow direct release into the environment and minimize the production of secondary wastes.

Research Progress and Implications

This report summarizes work after 6 months of a 3-year project. Several previously synthesized ligands containing between one and four Me-3,2-hydroxypyridinone (HOPO) groups (Fig.1) were thermodynamically characterized using Ce(IV) as a model for Pu(IV) coordination.

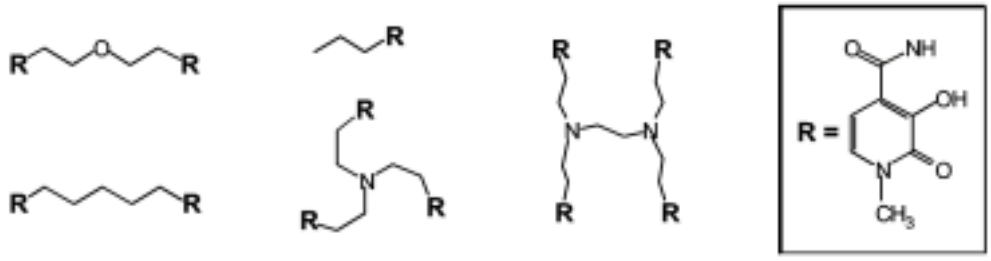

Figure 1. Structure of Me-3,2-HOPO amide ligands of various denticity.

The identical charges and nearly equal radii of Ce(IV) and Pu(IV) make the former ion an excellent model for the latter. Close parallels in the coordination and redox chemistry of these ions have been established previously. Ce(IV) offers a special advantage in modeling Pu(IV) complexation because of its electrochemistry which allows one to determine even very large formation constants for Ce(IV)

complexes from those of the corresponding Ce(III) complexes and the redox potentials of the Ce(IV)/Ce(III) pairs. Redox potentials were measured by both static methods (potentiometry) and kinetic methods (cyclic voltammetry and Osteryoung square wave voltammetry).

The stability constants for Ce(III) complexes were determined by either potentiometric or spectrophotometric titration. They are, to a good approximation, a linear function of the number of HOPO groups bound to the metal (the linear fit of log b versus the number of HOPO groups has a slope of 4.80 and an intercept of 1.33). Because of the much stronger coordination of Ce(IV) than Ce(III), only the overall stability constants for coordinatively saturated complexes of Ce(IV) (with 4 HOPO groups per metal ion) could be determined based on electrochemical methods. In all cases (with bi-, tetra-, hexa- and octadentate ligands), the formal potential for Ce(IV)/Ce(III) in such saturated complexes was approximately 1.6 V lower than the formal potential for the aqueous Ce^{4+}/Ce^{3+} pair (+1.7 V vs. NHE), meaning that the Ce(IV) complexes have stability constants approximately 27 orders of magnitude larger than those of the Ce(III) complexes. Since a typical value for a stability constant of a Ce(III) complex with 4 HOPO groups is 10^{20}, a typical one for complexes of Ce(IV) is 10^{47}. Calculations for Ce(IV) and the octadentate ligand (total metal concentration 10^{-6} M and total ligand concentration 10^{-5} M) lead to pM=46.0 at pH 7; 24.3 at pH 2 and 12.5 at pH 0. Given that similar numbers are expected for Pu(IV), these results imply that HOPO ligands are able to bind the metal strongly even at very low pH, and are therefore perfectly suited as extractants from acidic waste. As we have shown in a separate study, solid-supported ion exchange materials based on HOPO groups can extract Pu(IV) in up to 5 M HNO_3 with loading capacities of 70-90%.

Several complexes of Ce(IV) with the same ligands were synthesized from either organic solvents or water, and the structures of three of these complexes (with bidentate and tetradentate ligands) were determined by single crystal X-ray diffraction studies. In all these cases, a total of 8 oxygen atoms (2 from each HOPO group) were coordinated to the metal. Least-squares shape analysis of these complexes demonstrated that their coordination geometry may vary significantly (from nearly a trigonal dodecahedron to nearly a square antiprism) with subtle changes in the ligand backbone or when water was used instead of an organic solvent. The observed conformational flexibility implies that there are no rigorous steric requirements towards the ligand, and simple (bidentate) HOPO fragments attached to a flexible polymeric chain may be as affective as the octadentate ligand. This implication is corroborated by the similar formal potentials of all Ce(IV)/Ce(III) pairs (see preceding paragraph) and by tests of polystyrene-supported bidentate HOPO ligands with Pu(IV) conducted at LLNL.

Planned Activities

Part of our next efforts during this year will be directed towards the thermodynamic characterization of the extraction agents and polymer-based materials with HOPO ligands which have shown great promise as Pu(IV) sequestering agents (fast kinetics, stability in acidic and alkaline conditions, and high affinity for Pu(IV) in the presence of EDTA or Fe(III) in large excess). Another route of investigation will be the thermodynamic characterization of uranyl complexes of HOPO and catecholamide ligands, since the uranyl ion has very different coordination chemistry from that of Pu(IV). In the second year of this project, we plan to synthesize new liquid-liquid and polymer-supported extractants with improved properties and simplified preparation, based on our better understanding of their chemistry as a result of our studies.

Other Access To Information

Web page: **http://www.homestead.com/knr/HomePage.html**

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Cavitational Hydrothermal Oxidation: A New Remediation Process

Dr. Kenneth S. Suslick, University of Illinois at Urbana-Champaign

Research Objective

Our primary goal is to develop a quantitative understanding of cavitation phenomena in aqueous media and the development of applications of cavitation to remediation processes. Our efforts have focused on three separate areas: sonoluminescence as a probe of conditions created during cavitational collapse in aqueous media, the use of cavitation for remediation of contaminated water, and an addition of the use of ultrasound in the synthesis of novel heterogeneous catalysts for hydrodehalogenation of halocarbons under mild conditions.

Research Progress and Implications

This report summarizes work after one year of a three year project.

In order to gain further understanding of the conditions present during cavitation, we have continued our studies of sonoluminescence [1]. We have made recent breakthroughs in the use of emission spectroscopy for temperature and pressure measurement of cavitation events, which we expect to publish shortly. We have been able to measure *for the first time* the temperature of cavitation *in water* during multi-bubble cavitation in the presence of aromatic hydrocarbons [2]. The emission from excited states of C_2 in water gives temperatures that are consistent with adiabatic compressional heating, with maximum temperatures of 4300° K. Our prior measurements of cavitation temperatures in low vapor pressure nonaqueous media gave somewhat higher temperatures of 5000 K [1]. This work lays permanently to rest exotic mechanisms for cavitational chemistry, at least for cavitation fields.

In a new avenue of research, we have recently explored the generation of cavitation by hydrodynamic techniques and demonstrated for the first time that chemical reactions occur during turbulent flow of water and of water containing chlorocarbons [3]. This work received substantial publicity. While the chemical effects of *acoustic* cavitation (i.e., sonochemistry and sonoluminescence) have been extensively investigated during recent years, little is known about the chemical consequences of *hydrodynamic* cavitation created during turbulent flow of liquids. Hydrodynamic cavitation is observed when large pressure differentials are generated within a turbulent liquid flow and is accompanied by a number of physical effects, erosion being most notable from a technological viewpoint. It has the potential advantage of facile scale-up: there already exist commercial high pressure flow mixing units capable of generating hydrodynamic cavitation with flows of 50 gpm (Microfluidics, Inc., Newton, MA). However, prior reports of hydrodynamically induced chemistry or luminescence and direct comparisons to sonochemistry or sonoluminescence have been extremely limited. The oxidation of iodide to triiodide in aqueous solutions containing halocarbons (e.g., $CHCl_3$ or CCl_4) under hydrodynamic cavitation conditions was examined in order to determine the origin of this hydrodynamic chemical reaction. This reaction also serves as a model for remediation of halocarbon contaminated water using hydrodynamic cavitation, a previously unexplored approach to remediation. The effects of several experimental variables on the I_3^- production rate were investigated. Increasing the reaction temperature inhibits the I_3^- production due to increased vapor pressure, which leads to reduced efficacy during cavitational collapse; the rate decreases exponentially with vapor pressure. The production of I_3^- is sensitive to the nature of the dissolved gas and decreases exponentially with increasing gas thermal conductivity. Thus, the chemistry observed and its response to external parameters is remarkably similar to ultrasonically induced cavitation, albeit the sonochemical rates are significantly higher at least with our current experimental configurations.

Planned Activities

Our overall goal in this research is to develop our understanding of the reactions of organic compounds in the presence of high intensity ultrasound. To approach this goal, our planned activities will continue in three areas: 1) investigation of the local conditions formed during cavitation in water; 2) mechanistic examination of the effects of cavitation on aromatic hydrocarbons and halocarbons, and 3) determination of degradation yields as a function of experimental configurations for cavitation production with aromatics and halocarbons as toxic impurities in water. In all cases, we will continue our special emphasis on the mechanistic origins of sonochemistry, in relationship to its applications to environmental challenges. Information gained should lead to effective protocols and equipment for large scale treatment of contaminated water and soil.

We have also developed a new research area relevant to environmental remediation chemistry that derives from our recent discovery of the catalytic *hydrodehalogenation* of halocarbons. In work not funded by the DOE, we have been actively involved in the development of sonochemical preparations of active heterogeneous catalysts [4-6]. The localized hot-spot created during acoustic cavitation is sufficient to strip ligands completely from metal complexes. This process also produces enormous cooling rates ($>10^9$ K/s) and so allows the formation of colloidal, amorphous metal aggregates. We have very recently used ultrasound to produce nanostructured MoC_2 with very high surface areas and excellent catalytic activity [7]. Our most recent discovery is very relevant to our DOE project, however: this sonochemically prepared MoC_2 is an extremely effective and stable *hydrodehalogenation* catalyst. In gas flows with H_2, we can remove both Cl and F from essentially all halocarbons, replacing the halogen with hydrogen quantitatively and quickly without degradation of the MoC_2 catalyst (in spite of the release of HCl or HF which rapidly destroy most other catalysts), under mild conditions (<300° C). We have examined quantitatively the catalytic properties of supported catalysts produced sonochemically from using gas/solid microreactor kinetics monitored by GC/MS. We expect to publish this work in the near future.

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A Novel Energy-Efficient Plasma Chemical Process for the Destruction of Volatile Toxic Compounds

Dr. Lal A. Pinnaduwage, Oak Ridge National Laboratory

Research Objective

Removal of low-concentrations (below several percent) of volatile toxic compounds (VTCs) from contaminated air streams is encountered at DOE waste sites in two instances:

(1) Off-gases resulting from air-stripping of contaminated soils; and
(2) Effluent from the incineration of highly-concentrated combustible hazardous wastes

The objective of our research program is to develop a novel plasma chemical process for the destruction of VTC's in low-concentration waste streams.

Research Progress and Implications

Within the past year and a half, the basic physics/chemistry involved in the dissociative electron attachment to highly- excited molecules was unraveled in a plasma mixing apparatus:

L.A. Pinnaduwage, D.L. McCorkle, and W. Ding, "Enhanced electron attachment to highly excited molecules using a plasma mixing scheme", Appl. Phys. Lett. 71, 3634 (1997).

W. Ding, D.L. McCorkle, and L.A. Pinnaduwage, "Enhanced formation of negative ions by electron attachment to highly-excited molecules in a flowing afterglow plasma", J. Appl. Phys. (Submitted , 1998)

L.A. Pinnaduwage, "Implications of Electron Attachment to Highly-Excited States in Pulsed Power Discharges", 11th IEEE Pulsed Power Conference, Baltimore, Maryland, June 29- July 2, 1997.

W. Ding, D.L. McCorkle, and L.A, Pinnaduwage,"Enhanced Radical Formation by Electron Attachment to Highly-Excited States of Molecules in Plasmas", to be presented at the 25th IEEE International Conference on Plasma Science, Raleigh, North Carolina, June 1-4, 1998.

A methodology for the evaluation of VTC destruction in a plasma mixing apparatus was developed:

C.Y. Ma, D.L. McCorkle, W. Ding, L.A. Pinnaduwage, "A methodology for direct sampling and gas chromatographic/mass spectral analysis of volatile organic compounds emerging from a low- pressure, flow-through reaction cell", Anal. Chem. (submitted, 1998).

A baseline study on the destruction of VTC's using a DC glow discharge apparatus was completed:

D.L. McCorkle, W. Ding, C.Y. Ma, and L.A. Pinnaduwage, "Exploratory studies on a plasma remediation process based on enhanced dissociative electron attachment to highly-excited molecules", J. Phys. D.(Appl. Phys.) (submitted, 1998).

D.L. McCorkle and L.A. Pinnaduwage,"Destruction of CH_2Cl_2 Using a Glow Discharge Scheme", 50th Annual Gaseous Electronics Conference, Madison, Wisconsin, October 6-9, 1997.

W. Ding, D.L. McCorkle, and L.A, Pinnaduwage,"Decomposition of Volatile Organic Compounds in a Positive Column Glow Discharge Plasma", to be presented at the 25th IEEE International Conference on Plasma Science, Raleigh, North Carolina, June 1-4, 1998.

Two patent disclosures based on this work have been elected by the ORNL Technology Transfer Office to be filed:

L.A. Pinnaduwage, C.Y. Ma, D.L. McCorkle, and W. Ding, "Destruction of Low- Concentrations of Volatile Toxic Compounds using Glow Discharge"

L.A. Pinnaduwage, W. Ding, and D.L. McCorkle, "A Plasma Mixing Method and Device for Plasma Processing of Materials".

These concepts still need to be tested.

In order to expedite the destruction efficiency measurements, quite recently we have developed a direct sampling mass spectrometric process which avoids the usage of the time consuming gas chromatographic analysis. We will be using this new analysis method in our pulsed discharge experiments.

Planned Activities

The studies conducted so far have indicated that a pulsed discharge would enhance the destruction of VTC's compared to a DC discharge. We have purchased a pulsed power supply system and have just initiated pulsed discharge studies. (Anticipated time period: 1998-1999).

In order to clarify the mechanisms responsible for the enhanced destruction in pulsed discharges, we will conduct a diagnostic pulsed discharge experiment in a different apparatus. We believe that the additional enhancement observed in the pulsed discharges is due to two reasons:

(1) The destruction of metastable states by electron impact is reduced in the post discharge period; and
(2) Additional metastable states can be produced in the post discharge via dissociative recombination of electrons with dimer ions of the rare gas.

Therefore, the excitation transfer to the VTC molecules would be optimum in the post discharge period. If additional excitation of VTC molecules occurs in the post discharge period via the above processes, then dissociative electron attachment to those excited molecules will lead to an enhancement in negative ion formation in the post discharge. We will conduct a time resolved photodetachment experiment to verify the enhanced negative ion formation. (Anticipated time period: 1998-1999).

The studies we have conducted so far involved mixtures of VTCs in rare gases. In order to deal with realistic VTC mixtures in air, we will use the basic knowledge gained from the studies of 1 and 2 above in a plasma mixing scheme. In this case the rare gas metastable states produced will be mixed with VTC/N_2 mixtures first and then we will also study the influence of the humidity and the O_2 on the destruction process. Following these studies we will study contaminated air streams to assess the destruction efficiencies. (Anticipated time period: 1999-2002).

Photocatalytic and Chemical Oxidation of Organic Compounds in Supercritical Carbon Dioxide

Dr. Daniel M. Blake, National Renewable Energy Laboratory

Research Objective

1) To determine if photocatalytic or other clean oxidation chemistry can be applied to the removal of organic or inorganic contaminants that are introduced into supercritical carbon dioxide during its use as an extraction and cleaning medium in DOE environmental and waste minimization applications. The targets are those contaminants left in solution after the bulk of the solutes have been separated from the fluid phase by changing pressure and/or temperature (but not evaporating the CO_2). This is applicable to development of efficient separations of contaminants from the fluid stream and will strengthen pollution prevention strategies that eliminate hazardous solvents and cleaning agents.
2) To explore the use of supercritical carbon dioxide as a solvent for the photocatalytic oxidation of organic compounds and to compare it to other types of oxidation chemistry. This will add to the fundamental understanding of photocatalytic oxidation chemistry of particulate semiconductors and provide new knowledge about conditions that may have relevance to the chemical fixation of carbon dioxide under photocatalytic conditions.

Research Progress and Implications

This report summarizes the results of work done during the first 1.3 years of a three year project. During the first nine months effort focussed on the design, construction and testing of a closed recirculating system that can be used to study photochemistry in supercritical carbon dioxide at pressures up to 5000 psi and temperatures up to about 50° C. This was followed by a period of work in which the photocatalytic oxidation of benzene and acetone in supercritical, liquid, and gaseous carbon dioxide containing dissolved oxygen was demonstrated. The photocatalyst was titanium dioxide supported on glass spheres. This was the first time it was possible to observe photocatalytic oxidation in a supercritical fluid and to compare reaction in the three fluid phases of a solvent. This also demonstrated that it is possible to purify supercritical and liquid carbon dioxide using photochemical oxidation with no chemical additions other than oxygen.

The oxidation of benzene produced no intermediates detectable using on line spectroscopic analysis or by gas chromatographic analysis of samples taken from the flow system. The catalyst surface did darken as the reaction proceeded indicating that oxidation products were accumulating on the surface. This is analogous to the behavior of aromatic compounds in air phase photocatalytic oxidation. The reaction of acetone under similar conditions resulted in the formation of low levels of by-products. Two were identified as products of the reaction of acetone with itself (4-methyl-3-penten-2-one and 4-hydroxy-4-methyl-2-pentanone) using gas chromatography with a mass spectrometer detector. Two other by-products also appear to be from the self-reaction of acetone. By-products of this type had not been observed in prior studies of the gas-phase photocatalytic oxidation of acetone. The by-products that have been observed can also be oxidized under the treatment conditions.

The above results establish that photocatalytic oxidation of organic compounds in supercritical carbon dioxide can be achieved. Until recently it was not possible for us to obtain high quality, quantitative kinetic data. The original flow cell used to obtain UV-Visible spectra on the recirculating fluid did not provide quantitative concentration data because the sapphire windows did not have adequate transmission characteristics below about 240 nm. A pair of windows with better transmission properties arrived as this report was being prepared.

While waiting for the replacement windows for the flow cell, the concentration of reactants was monitored by withdrawing samples of the fluid stream for gas chromatographic analysis. This allowed progress to be made in determining some of the factors that affected the rates of reaction in a qualitative sense but the results had large error bars due to the difficulty in obtaining reproducible samples from the pressurized system using gas tight syringes. This problem was recently solved by incorporating a gas chromatograph with automatic sampling valves into the flow system.

The two on line analytical methods will now result in reliable analytical data that can be used to follow the reaction kinetics and detect and identify reaction intermediates and by-products, if any are formed.

Planned Activities

During the next four months of work quantitative kinetic data will be obtained for the photocatalytic oxidation of benzene, acetone, and ethanol in supercritical, liquid, and gas phase carbon dioxide. The nature of species adsorbed on the catalyst surface will be explored using extraction and analysis by ion chromatography or high pressure liquid chromatography. This work will be done in collaboration with chemists at the University of Colorado at Denver. Later work will compare the results of the photocatalytic oxidation with thermal oxidation in supercritical carbon dioxide and test compounds that model those found in cleaning operations that use liquid or supercritical carbon dioxide.

Utilization of Kinetic Isotope Effects for the Concentration of Tritium

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Research Objective

The objective of this research program is to develop methods for concentrating tritium in water based on large primary isotope effects in catalytic redox processes. Basic research is being conducted to develop the chemistry of a complete cyclic process. Because tritium (generally present as HTO) is in a rapidly established equilibrium with protio-water, it moves with groundwater and separation from water cannot be achieved by the usual pump-and-treat methods using sorbants. The general methodology developed in this work will be applicable to a number of DOE waste streams, and as a consequence of the process tritium will be incorporated into an organic compound that will not readily exchange the tritium with groundwater. We intend to develop a process to remove tritium from H_2O by concentrating it with respect to protio-water. This research involves developing chemical cycles that produce high concentration factors for HTO and T_2O based on the discrimination of C-H and C-T bonds in oxidation reactions. Several steps are required in a cyclic process for the concentration of tritium in water. In the first step the tritium is incorporated in an organic compound. H-T discrimination occurs as the tritium containing compound is oxidized in a step involving a Ru(IV) oxo complex. Strong primary kinetic isotope effects lead to the oxidation of C-H bonds in preference to C-T bonds, and this reaction leads to concentration of tritium in the organic compound. The reduced form of the ruthenium compound can be reoxidized so that the oxidation step can be made catalytic.

Research Progress and Implications

Progress has been made along several fronts in the first 21 months of this project with much of the work directed toward demonstrating the individual steps required for the concentration of tritium in water. An early research objective is to carry out a proof-of-principle “cold” experiment in which the electrochemical reduction of carbon dioxide in an aqueous solution containing deuterium shows the incorporation of deuterium in the product substrate. This will be coupled to the catalytic oxidation of the formate anion demonstrating the fractionation of the deuterated component in a mixture of proteo- vs. deutero-organic compounds. The ruthenium(IV) oxo species chosen for this early work was the complex $[Ru(IV)(terpy)(bpy)O]^{2+}$ where terpy is 2,2',2''-terpyridine. In terms of more long range goals, additional themes have been explored. One is a continuing investigation of the magnitude of kinetic isotope effects to identify the most promising metal catalytic system. The second is to develop the catalytic chemistry in redox active films and membranes appropriate for device applications. The third general theme is to evaluate C-H/C-T kinetic isotope effects in the oxidation of several functionally different organic substrates by various Ru(IV) oxo complexes.

Tritium kinetic isotope effects are unknown, but they are expected to be as high or higher than the deuterium effect. Work is in progress to measure the tritium isotope effect for the oxidation of formate anion to carbon dioxide with $[Ru(IV)(terpy)(bpy)O]^{2+}$. The deuterium kinetic isotope effect (k(C-H)/k(C-D)) for oxidation of formate by $[Ru(IV)(terpy)(bpy)O]^{2+}$ was observed to be 25 which is comparable to but larger than the ratio measured by Roecker and Meyer (kH/kD = 19) while the value of the rate constant for oxidation of protio-formate was 3.85 M-1s-1 also in good agreement with the value reported by Roecker and Meyer for oxidation of formate by $[Ru(IV)(bpy)2(py)O]^{2+}$ (4.2 M-1s-1). Measurement of the kinetic isotope effect for oxidation of tritiated formate anion is in progress with measurements being made at the tracer level by measuring the rate of transfer of tritium from the formate anion to HTO. The concentration of tritium in water is being determined by

scintillation counting. Preliminary results indicate the tritium isotope effect is larger than the deuterium effect as expected. The formate anion is an attractive substrates for a "cold" demonstration involving the removal of deuterium from water because the tritiated formate anion can be separated by ion exchange from the reaction mixture. We have been able to confirm reports in the literature that CO_2 is reduced to formate at an indium electrode. We anticipate that large levels of formate can be generated by electrolysis, and this will be important for reducing the number of stages needed to effect a separation. Work is in progress to demonstrate the fractionation of deuterium by observing the build up of deuterated formate in the catalyzed oxidation of a mixture of deutero and proteo-formate. We have investigated the electrochemical kinetics of the Ru(III)/Ru(IV) redox reaction using cyclic voltammetry and utilizing an chemically modified electrode. Previous results have shown that it is very difficult to observe the III/IV redox couple on a glassy carbon electrode because of kinetic sluggishness. However, we observed found that an ITO electrode coated with Ru(terpy)((4,4`-($PO_3H_2$)-bpy)$(H_2O)^{2+}$ enhanced the response of the III/IV redox wave during a cyclic voltammetric experiment in which Ru(terpy)(bpy)$(H_2O)^{2+}$ dissolved in solution was undergoing oxidation. ITO electrodes coated with $TiO_2$ and [Ru(IV)(terpy)((4,4`-PO_3H_2)bpy)O]$^{2+}$ have also been used to study the catalyzed oxidation of benzyl alcohol and these electrodes with a surface immobilized catalyst were found to be active. Finally, a deuterium kinetic isotope effect of 61 has been observed for the second stage in the oxidation of benzyl alcohol by the Ru(VI) oxidant, trans-[Ru(VI)(tpy)(O)2(S)]$^{2+}$(S = CH_3CN). This is part of a systematic effort to identify catalyst-substrate combinations that maximize the isotope effect.

Planned Activities

By the end of FY 1998, we plan to complete a preliminary determination of the kinetic isotope effect for oxidation of formate by the complex [Ru(IV)(terpy)(bpy)O]$^{2+}$, and these results will be reported at the American Chemical Society Meeting in Boston. Following our report on the formate based fractionation experiments in the literature, we hope to be able to report the experimental realization of a complete cyclic system for deuterium separation from water. Other suitable substrate/electrode combinations for cyclic reduction /oxidation will be investigated. Use of electrodes with the Ru catalyst bound to the surface are highly desirable, and they will be further investigated.

Other Access To Information

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An Alternative Host Matrix Based on Iron Phosphate Glasses for the Vitrification of Specialized Nuclear Waste Forms

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Research Objective

Certain high level wastes (HLW) in the U.S. contain components such as phosphates, heavy metals, and halides which make them poorly suited for disposal in borosilicate glasses. Iron phosphate glasses appear to be a technically feasible alternative to borosilicate glasses for vitrifying these HLWs. The iron phosphate glasses mentioned above and their nuclear wasteforms are relatively new, so little is known about their atomic structure, redox equilibria, structure-property relationships, and crystallization products and characteristics. The objective of this research is to gain such information for the binary iron-phosphate glasses as well as iron phosphate wasteforms so that a comprehensive scientific assessment can be made of their usefulness in nuclear waste disposal.

Research Progress and Implications

This report summarizes the work undertaken and completed in the first 20 months of a three year (9/15/96 - 9/14/99) project (DOE Contract # DOE96ER45617). Approximately 250 samples, binary iron phosphate glasses and iron phosphate glasses containing one or two common nuclear waste components such as UO_2, Na_2O, Bi_2O_3, Cs_2O, SrO, and MoO_3, have been prepared. Weight loss has been used to measure the chemical durability and the redox equilibria between Fe(II) and Fe(III) has been investigated using Mössbauer spectroscopy. The atomic structure has been investigated using a variety of techniques including Mossbauer, Raman, X-ray absorption (XAS), and X-ray photoelectron (XPS) spectroscopies and neutron/high energy X-ray scattering. Glass forming and crystallization characteristics have been investigated using differential thermal analysis (DTA). In addition, information necessary for glass manufacturing such as suitable refractories and Joule heating parameters also have been obtained.

Productive research collaborations have been successfully established with the *Stanford Synchrotron Radiation Laboratory, Lawrence Berkeley National Laboratory, Argonne National Laboratory*, and the *Naval Research Laboratory*. The effect of radiation on iron phosphate glasses is being studied at the *Pacific Northwest National Laboratory* while the electrical conductivity is being measured at the *Ruder Boscovic Institute*, Croatia.

1. Chemical durability

In contrast to conventional phosphate glasses, the chemical durability of iron phosphate glasses is comparable to or better than that of borosilicate glasses. Considerable amounts, up to 35 wt% in certain cases, of waste components mentioned above can be present in iron phosphate glasses with no deterioration in the chemical durability. In addition, iron phosphate glasses can contain large amounts of selected simulated sludges. For example, iron phosphate wasteforms containing up to 60 wt% of a phosphate rich waste from tank C-112 at Hanford have been prepared.

2. Redox Equilibria

Irrespective of the valence state of iron ions in the starting batch, a redox equilibria corresponding to a Fe(II)/[Fe(III)+ Fe(III)] ratio of 0.2 to 0.3 is reached when melted under normal conditions, i.e. in air at 1100 -1200°C for 1-2 h. The process by which the redox equilibria is reached appears to be independent of the oxygen content in the melting atmosphere. However, the Fe(II) content in the glass can be increased beyond the equilibrium value by increasing the partial pressure of a reducing gas in the melting atmosphere or by increasing the melting temperature. The glass forming ability of iron phosphate melts is reduced considerably when the Fe(II) fraction exceeds 0.5. Additions of UO_2 or MoO_3 reduce the Fe(II) fraction in the glass, as compared to the base glass, whereas, Na_2O, Cs_2O, SrO, or Bi_2O_3 causes an increase in the Fe(II) content. Under normal melting conditions, none of the waste components cause the Fe(II) fraction to exceed 0.5, the value above which the glass forming ability decreases.

3. Atomic Structure

a.) Mössbauer Spectroscopy: Mössbauer hyperfine parameters measured for the binary iron phosphate glasses and their simulated wasteforms indicate that both species of iron ions are six-fold coordinated with near neighbor oxygens. Neither the isomer shifts nor the quadrupole splittings depend appreciably on the type or the concentration of the waste elements indicating that the addition of waste elements do not alter the local environment of the iron ions. It is reasonable to assume that the waste elements are situated outside the second coordination shell of iron ions.

b.) X-ray Absorption Spectroscopy (EXAFS/XANES): Fe-K edge EXAFS data suggest that the majority of oxygen ions in iron phosphate glasses are bonded via -Fe-O-P- links instead of via -P-O-P- links. This difference in the structural role of oxygen is believed to be the reason for the superior chemical durability of iron phosphate glasses. EXAFS data for the iron phosphate waste forms supports an atomic structure where the near neighborhood of the iron ions is unaffected by the addition of waste elements.

c.) X-ray Photoelectron Spectroscopy (XPS): O1s XPS spectra show that two types of oxygen ions are present, namely bridging (-P-O-P-) and non-bridging (-Fe-O-P- etc.) oxygens. In agreement with EXAFS measurements, only a minority of the oxygens appear to be bonded via -P-O-P- links. The addition of waste elements does not appreciably affect the bridging to non-bridging oxygen ratio.

d.) Raman Spectroscopy: Raman spectra of iron phosphate glasses studied herein are consistent with a P-O network dominated by $P_2O_7^{-4}$ dimer units instead of by PO_4^{-3} monomer units, in good agreement with EXAFS and XPS measurements. Major features in the Raman spectra do not change with the addition of waste components indicating that the P-O network is not disturbed by the waste elements.

e.) Neutron and High Energy X-Ray Scattering: Radial distribution functions obtained from neutron and high energy X-ray scattering suggest that the waste elements probably occupy Avoids@ in the glass structure without appreciably disturbing the -Fe-O-P- network.

4. Crystallization and Glass Forming Characteristics

Binary iron phosphate glasses possess a glass transition temperature of approximately 500°C and display two crystallization peaks in the DTA thermogram at approximately 580 and 775°C. Adding UO_2, SrO, or MoO_3 suppresses the crystallization tendency, but, at concentrations > 15 mol% Na_2O and Cs_2O promotes crystallization. None of the waste components lowers the glass transition temperature below 400°C, the acceptable lower limit for a vitrified wasteform.

5. Glass Manufacturing

a.) Refractories: Even though most phosphate glasses are highly corrosive to common commercial refractories, commercial alumina, zircon, or chrome refractories can be used to melt iron phosphate glasses and their waste forms. Under practical melting conditions, i.e in air at

1100°C, the corrosion rate of alumina, zircon, or chrome refractories was below 0.33 mm/day when tested in three different iron phosphate wasteform melts.

b.) Joule Heating: The AC conductivity of iron phosphate melts is suitable for Joule heating. The addition of waste elements, especially simulated sludges, further increases the conductivity.

Planned Activities

The analysis of the data obtained by the techniques mentioned above will be completed within the next 4-6 months. During the remaining time of this project, the main focus will be on iron phosphate glasses containing simulated HLWs. During this time, iron phosphate glasses containing simulated waste will be prepared and their atomic structure, redox equilibria, structure-property relationships, crystallization products and characteristics, and glass manufacturing processes will be investigated. We intend to acquire the compositional, property, and melting process information that is needed to evaluate the potential usefulness of iron phosphate wasteforms.

Other Access To Information

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Web Access

More information on this research is available at **http://www.umr.edu/~gkmars/emsp.html.**

Measurements and Models for Hazardous Chemical and Mixed Wastes

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Research Objective

Aqueous waste of various chemical compositions constitutes a significant fraction of the total waste produced by industry in the United States. A large quantity of the waste generated by the U.S. chemical process industry is waste water. In addition, the majority of the waste inventory at DoE sites previously

used for nuclear weapons production is aqueous waste. Large quantities of additional aqueous waste are expected to be generated during the clean-up of those sites. In order to effectively treat, safely handle, and properly dispose of these wastes, accurate and comprehensive knowledge of basic thermophysical property information is paramount. This knowledge will lead to huge savings by aiding in the design and optimization of treatment and disposal processes. The main objectives of this project are:

- Develop and validate models that accurately predict the phase equilibria and thermodynamic properties of hazardous aqueous systems necessary for the safe handling and successful design of separation and treatment processes for hazardous chemical and mixed wastes.
- Accurately measure the phase equilibria and thermodynamic properties of a representative system (water + acetone + isopropyl alcohol + sodium nitrate) over the applicable ranges of temperature, pressure, and composition to provide the pure component, binary, ternary, and quaternary experimental data required for model development.

Research Progress and Implications

As of May, 1998, nine months into the first year of a three year project, we have made significant progress in the database development, have begun testing the models, and have been performance testing the apparatus on the pure components.

Database Development: An extensive literature search has been completed and the data are being compiled in a database on the internet shared by NIST and MTU. The database includes the vapor pressures, densities, and permitivities of the pure solvents; and the VLE, densities, and activity coefficients of the mixtures. It also includes a literature search on liquid phase activity models used with these systems. Over 150 data and several dozen modeling articles have been obtained. Data of the highest quality are being used to test the models for the system under study. The gaps in the data and areas where our measurements should be concentrated are being identified and evaluated.

Model Development: Two models are being investigate by NIST and MTU. The NIST model concentrates on the phase equilibria and coexisting densities and the MTU model concentrates on the liquid phase activities. The model under development at NIST for the phase equilibria and the densities of the coexisting phases uses the Peng-Robinson-Stryjek-Vera cubic equation of state for both the liquid and vapor phases. The density correction of Mathias et al.[1] is applied to the liquid density. The Wong-Sandler mixing rule is employed, with the NRTL used for activity coefficient contributions to the mixing rules. This allows the cubic equation of state to be used for mixtures containing ions and other nonvolatile species. The computer program to implement this overall model has been written, and nonlinear least squares programs have been written to optimize the parameters for the model. A test of the model with saturation pressure data for the pure solvents (water, acetone, and isopropyl alcohol) gives a deviation of less than 0.2%.

The model under development at MTU for the liquid phase activities uses the UNIFAC or UNIQUAC parameters. The models are being evaluated with the preliminary database.

Experimental Measurements: The data for this project are measured on three different apparatus. The three apparatus required are an ebulliometer at MTU, a high temperature/high pressure phase equilibria apparatus at NIST for azeotropic aqueous-organic-salt mixtures, and a coexisting density and vapor-liquid equilibrium apparatus at NIST. The activity coefficients from the ebulliometer measurements will be validated with the activity coefficients calculated from the vapor-liquid equilibrium data.

The calibrations have been completed for the NIST apparatus. The performance tests on these apparatus are nearly complete. A new high-accuracy low-pressure pressure transducer was acquired for these experiments. The ebulliometer at MTU is being modified. Temperature, pressure and composition calibrations for the ebulliometer are nearly complete. Measurements of the vapor pressures and coexisting densities of water, acetone, and isopropyl alcohol from 280 to 400 K are nearly complete.

[1] P.M. Mathias, T. Naheiri, and E.M. Oh. 1989. "A Density Correction for the Peng-Robinson Equation of State", *Fluid Phase Equilibria* 47: 77-87.

Planned Activities

Upon completion and verification of the pure component measurements, VLE and densities of the binary water+solvent mixtures on the NIST apparatus will be measured and completed by Fall of this year. The data will cover the temperature range of 275 to 425° K at pressures to 14 Mpa. Next year, measurements of the VLE and densities of the ternary water+solvent mixtures and binary water+salt mixtures will begin on the NIST apparatus. The activity coefficients measurements of the binary systems will begin on the MTU ebulliometer. In the final year, the VLE and densities of the ternary and quaternary water+solvent+salt mixtures will be measured on the NIST apparatus and their activity coefficients will be measured on the MTU ebulliometer. All of the measurements will be completed about 2.5 years into the project, and the optimization and tests of the models will be completed by the end of the three year project. The model for phase equilibria predictions will be further optimized and tested for the following systems and properties:

- Solvent mixture bubble point pressures. (Some data are available now.)
- Pure solvent and solvents mixture densities. (Some data are available now.)
- Water+solvent+salt mixture vapor pressures and densities. (Most of these data need to be measured before testing.)

Isolation of Metals from Liquid Wastes: Reactive Scavenging in Turbulent Thermal Reactors

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Research Objective

The objective of this project is to develop the fundamental science base necessary to assess the utility of high-temperature processes to volatilize metals in DOE metal-bearing liquid wastes, so that they can be reactively scavenged by sorbents. The problem is addressed through a collaborative research program involving a team of five senior scientists and their respective laboratories, at four institutions.

Specific goals are to:

1.) Understand high-temperature reaction kinetics between sorbent substrates and certain volatile and semi-volatile metals in the DOE liquid waste inventory (e.g., Cs and Sr), using a laminar-flow reactor for which extraction of kinetic data is not complicated by turbulence;
2.) Develop models to predict both trajectories of individual droplets in turbulent high-temperature reactors, and rates of metal evolution from droplets, and compare model predictions with experimental data from a pilot-scale turbulent thermal reactor;
3.) Connect the reaction kinetic models with the droplet trajectory/mass evolution models, in order to predict and optimize metal scavenging processes in turbulent-flow reactors, and to test these combined models against data taken from a turbulent high temperature reactor.

Research Progress and Implications

This report summarizes work at a point midway through the first year of a 3-year project.

At the University of Arizona (UA), two tasks are underway. The first task is concerned with attempting to understand high-temperature reaction kinetics between sorbent substrates and certain volatile and semi-volatile metals. The second task is concerned with applying Kerstein's One Dimensional Turbulence model to prediction of droplet trajectories in turbulent flow.

A UA doctoral student has commenced working on the first task. The high temperature laminar-flow reactor has been refurbished and is now available for screening tests. Nonradioactive isotopes of cesium and strontium were chosen as representative metals of interest to DOE. Kaolinite was chosen as a representative sorbent, since its interactions with alkali metals such as sodium and potassium have already been studied in this laboratory. The metals are introduced as aqueous solutions of cesium acetate and strontium nitrate and the metal-containing solution is then sprayed through a natural gas flame. The metal vaporizes, and then either reacts with sorbent substrates or nucleates and condenses further downstream. For the screening tests, which are about to commence, particulate samples are isokinetically withdrawn at the end of the reactor, and passed through a Berner low pressure impactor for size fractionation into multiple sub-micron and super micron aerodynamic size classes. The size-segregated distribution of cesium or strontium then allows the extent of scavenging by sorbent to be inferred.

We have conducted a multi-component equilibrium analysis on the partitioning of cesium and strontium at high temperatures. Prediction of dewpoints is important, since only the metal vapors will react with sorbents. Taken from the most recently updated thermodynamic data available, the strontium compounds considered were: Sr, SrCl, $SrCl_2$, SrO, SrOH, $Sr(OH)_2$, SrS, Sr(s), Sr(l), $SrCl_2$(s), $SrCl_2$(l), SrO(s), SrO(l), $Sr(OH)_2$(s), $Sr(OH)_2$(l), SrS(s). The cesium compounds considered were: Cs, CsCl, CsO, CsOH, Cs_2, Cs_2Cl_2, Cs_2O, $Cs_2(OH)_2$, Cs_2SO_4, Cs(s), Cs(l), CsCl(s), CsCl(l),CsOH(s), CsOH(l), Cs_2SO_4(s), Cs_2SO_4(l). In the absence of chlorine, 100 ppm strontium began to condense at 2000K, with condensation complete at 1500K. Addition of 2500 ppm chlorine reduced the dewpoint to 1410K. Hence, chlorine addition may be required to facilitate strontium capture by sorbents, a procedure which has been shown to be effective for the scavenging of nickel, which is a similarly refractory metal. Sulfur had little effect on strontium dewpoints. 100 ppm of cesium began to condense at a very low temperature of 700 K. Although chlorine and sulfur both increased the condensation dewpoints to 900K and 1300K respectively, these predictions suggest that cesium would be an excellent candidate for sorbent scavenging.

A laser diagnostic system, to allow in-situ measurement of solid, droplet, and vapor metal species has been designed by the University of Illinois (UI) for use with the UA laminar flow reactor. Optical components and arrangements have been specified which will provide illumination sheets 5 cm across and less than 100 microns thick for probing the spatial distribution of droplets, soot, OH radical, free aluminum atoms, and free copper atoms. Additional components also allow for laser-induced breakdown at a fixed position within this sheet. Design is nearly complete and fabrication of the system has started. Work has begun on designing modifications to the reactor, to allow optical access and to ensure safe and secure operation. A soon to-be-appointed post-doctoral research associate, to be supervised by UI, will be responsible for the operation of the laser and related spectroscopic apparatus, and the extraction of data from the UA reactor. Two meetings, one at UA and one at UI, have enabled this task to advance. A third meeting at EPA in North Carolina helped ensure that the design of system to be used at UA is also compatible with the larger turbulent flame reactor at EPA.

A meeting between Dr Kerstein and Professor Wendt in October initiated modeling activities for the second task. A graduate student at UA is now collaborating with personnel at Sandia National Laboratories (Livermore) and will spend six weeks this summer working with Dr. Kerstein and his team there. Efforts hitherto have focussed on becoming familiar with Kerstein's One Dimensional Turbulence Model and with using the UA mini supercomputer cluster.

Computational work at Illinois focuses on the development of models for computing the trajectories of evaporating drops over a wide range of initial sizes, including drops large enough for deformation and inertial effects to be important. To that end, we have extended our earlier computations of axisymmetric drop motion to the case where the drop density is much larger than that of the surrounding

medium, and found that elongated prolate drops can occur in this case. Work is underway to account for drop acceleration and heat transfer in the finite-element code.

Planned Activities

The UA screening tests for scavenging of cesium and strontium by kaolinite should be complete by the end of the first year. Fabrication of the optical diagnostic system should also be one third complete at the end of the first year. Preliminary calculations using the One Dimensional Turbulence Model to predict droplet trajectories in turbulent flows should be well underway by the end of the Summer. Modeling work will continue throughout the duration of the project.

Processing of High Level Waste: Spectroscopic Characterization of Redox Reactions in Supercritical Water

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Research Objective

We are engaged in a collaborative research effort with Los Alamos staff scientists Steven Buelow, Jeanne Robinson, and Bernie Foy– all staff members in group CST-6. The work proposed by these LANL staff scientists is directed towards the destruction of complexants and oxidation of chromium and technetium by hydrothermal processing in near critical or supercritical aqueous solutions. Our work addresses two areas of investigation related to ongoing efforts at LANL:

1. Kinetic studies of oxidation-reduction reactions in supercritical water.
2. Measurement of physical properties of ionic solutes in supercritical water.

Research Progress and Implications

All of the work during this first year was carried out at Los Alamos National Lab. During the Summer program at LANL all equipment and supplies were provided through Dr. Buelow's program at LANL. We have now set up a Raman spectroscopy lab at Furman. Using departmental funds we purchased an optical bench, a laser, and a CCD detecto, and a grant from the Dreyfus Foundation assisted in the purchase of a Raman spectrometer. We are now able to carry out experiments using the Raman system at Furman. Our plan is to continue the Summer collaboration at LANL and carry out experiments at Furman during the academic year.

During the Summer of 1997 the PI and two undergraduate students from Furman worked for 10 weeks at Los Alamos National Lab. Dana Olsen is a senior chemistry major, and Robb Lanning a junior chemistry major. The research was conducted in collaboration with Steven J. Buelow, a staff scientist in Group CST-6. Our EMSP grant was written as a collaborative program of research with Dr. Buelow, continuing an association of six years.

The first two weeks of the Summer program were spent setting up the Raman spectrometer system with a high temperature–high pressure cell. Initial experiments examined the reaction of nitrate anion with organic species such as ethanol and acetate anion. These early experiments gave erratic results because of high levels of scattered light from the Raman cell caused by particle formation at high temperatures.

Beginning with the third week we began working more directly with Dr. Buelow and a post doctoral fellow and graduate student who were working on his EMSP project. This goal of this project is to find ways of removing Cr(III) compounds from Hanford tank wastes before the solids are formed into glass ingots for permanent storage. High chromium content results in imperfect, cracked glass ingots.

Our efforts began with an examination of spectroscopic methods for characterization of solids formed when Cr(III) solutions are made basic. The chemistry of chromium in basic solutions is amazingly complex with hydroxides and oxides present in varying degrees of oligomerization. It is important to learn how the history of the sample affects the distribution of products, especially the temperature of the solution and its pH. A number of experiments were carried out on seven samples prepared in the laboratory. These samples were prepared by Dr. Ding, the post doctoral fellow, following literature procedures to make $Cr(OH)_3$, CrO(OH), and Cr_2O_3. Other samples were prepared then calcined at various temperatures up to 700° C. We determined that infrared spectra of the samples in KBr pellets provided the most reliable diagnostic information in a short time. Both Raman spectra and X-ray photoelectron spectra provided some structural information but were not as useful as IR spectra. The IR spectra indicated the presence and relative amounts of $Cr(OH)_3$, Cr_2O_3, and CrO_4^{2-}. We also observed a band attributed to carbonate, which forms when carbon dioxide is absorbed from the atmosphere by the basic solution.

Along with these spectroscopic characterization studies we began experiments on the dissolution and oxidation of chromium (III) compounds. All of the samples prepared by Dr. Ding were treated by several different methods. Visible spectra of samples treated with DI water and filtered showed the presence of chromate in the water for samples calcined at 200° C or higher. None of the Cr(III) compounds dissolved. The same samples were stirred with aqueous solutions of oxalic acid. No additional solubility was noted with oxalic acid.

All of the samples showed rapid reaction with basic hydrogen peroxide solutions with formation of yellow supernatant solutions. Quantitative results were obtained for the fraction of each sample dissolved in this treatment. Infrared spectra of the remaining solid showed that everything except Cr_2O_3 was dissolved in this reaction.

A number of experiments were conducted to determine if Cr(III) compounds could be oxidized by NO_3^- in high temperature water. These reactions were carried out in the high temperature Raman cell. In none of the experiments did we observe a decrease in the intensity of the nitrate band at 1050 cm^{-1}, nor did we see the chromate band at 850 cm^{-1} grow in. The dark green color of the solutions reduced the intensity of scattered Raman light, and formation of solids above 300 ^oC blocked the laser beam at the lower diamond window.

Dana Olsen followed the change in pH as $Cr(NO_3)_3$ was added to NaOH solutions of in an attempt to learn something about the stoichiometry of chromium hydroxide formation. She found that in the early stages more than 4 hydroxides reacted with chromium. The final stoichiometry was convincingly close to the 1:3 ratio expected for $Cr(OH)_3$.

Robb Lanning studied the kinetics of the reaction of Cr(III) with basic hydrogen peroxide by following the change in pH as the reaction proceeds. The data he generated at different concentrations of reactants convince us that the reaction is complex and not easily interpreted in terms of a simple order rate equation.

In the course of Robb's experiments we noted that the addition of NaOH to H_2O_2 resulted in the reduction of the O-O stretch band and appearance of a new band, which we tentatively assign to the HO_2^- anion. We have been unable to find a literature reference to the Raman spectrum of this species. We will carry out the experiment with D_2O_2 to confirm this assignment. If this assignment proves to be legitimate, we will submit a note to the *Journal of Physical Chemistry*.

Planned Activities

During the Summer of 1998 two students will work with the PI at LANL. We will continue to investigate the oxidation of Cr(III) in basic solution using various oxidizing agents. The nitrate ion is the most attractive oxidant because of its presence in Hanford tank wastes. In addition to Raman spectroscopic probes of the reaction we will use ultra violet absorption of the nitrate ion to follow the

kinetics of reaction. Our goal is to obtain reliable reaction rates and to establish the rate equation for several redox reactions in the temperature range of 250° C to 400° C. We will continue the study of the Raman spectrum of HO_2^-. Recent experiments in which we made the deuterated species showed the same wavenumber for the O-O stretching vibration. We are carrying out ab initio caculations to help in the assignment of this band.

Acid-Base Behavior in Hydrothermal Processing of Wastes

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Research Objective

A new technology, hydrothermal oxidation (also called supercritical water oxidation), is being developed to treat high level nuclear wastes. Nitrates are reduced to nitrogen; furthermore, phosphates, alumina sludge, and chromium are solubilized, and the sludge is reconstituted as fine oxide particles. A major obstacle to development of this technology has been a lack of scientific knowledge of chemistry in hydrothermal solution above 350 C, particularly acid-base behavior, and transport phenomena, which is needed to understand corrosion, metal-ion complexation, and salt precipitation and recovery. Our objective is to provide this knowledge with in-situ UV-vis spectroscopic measurements and fully molecular computer simulation.

A major objective of the experimental studies has been to determine the equilibria for Cr(VI) up to 420° C as this is a key species to be removed from nuclear wastes. A wide range of concentrations of KOH and perchloric acid were utilized to manipulate the acid-base equilibria and to understand the effects of ion solvation and ion pairing. The second system is the equilibria between nitric acid, nitrous acid, nitrogen dioxide, nitrite and nitrate ions and oxygen. For both of these systems, chemical equilibria has not been measured previously in hydrothermal solution at these temperatures.

On the theoretical side, we have focused on the study of the transport properties of aqueous ions in supercritical water. The motivation for these studies is two fold. First, although transport coefficients are fundamental to solution chemistry reaction rates, the behavior of such transport properties over wide ranges of density and temperature are not well established experimentally, particularly at the densities typically of interest (< 0.5 g/cc). Second, due to practical challenges, ionic association equilibria in SCW is typically accessed via measurements of conductivity followed by analysis through a theoretical model that incorporates ion pairing. The results of these analyses in the interesting low density region have yielded results for the limiting infinite dilution conductivity of alkali halides which are not consistent among labs. However, the most common result suggests a nearly constant ionic diffusion constant with decreasing density, which is further rather insensitive to temperature. This is in contrast to the typical behavior at higher densities, where there is agreement on a linear increase with decreasing density. Either this surprising behavior is a physical result of a balance of forces that is different at the lower densities, or the model used to extrapolate to infinite dilution, and to extract the association constants, is not accurate for these cases. Our goal is to determine independently via computer simulation what one should expect of these transport coefficients.

Research Progress and Implications

This report summarizes work after the second year of a 3-year project. Equilibria of nitric acid in supercritical water (SCW) were studied by using UV-Vis spectroscopy. It was found that nitric acid

reversibly decomposes in supercritical water (380 - 400° C) to form NO_2, nitrous acid, nitrite ion and oxygen. The extent of decomposition increases with temperature. The reaction occurs to an immeasurable degree in pure sodium nitrate solution which demonstrates that the acidic medium is necessary for decomposition. At constant temperature, the contribution of nitrogen in the +3 oxidation state versus that in the +4 oxidation state (nitrogen dioxide) increases with increasing pressure (density).

To model transport coefficients, we have taken two different approaches. In the first (see publication list), we have used a model of solvent induced friction to infer ionic transport. The model assumes that the viscosity of the solvent is different in the first solvation shell of the ion compared to the bulk, a division of the solvent that we have earlier demonstrated captures the main elements of solvation thermodynamics. Simulation of solvent rotational dynamics is used as a measure of the excess viscosity in the region near the ion, from which one can infer a radial viscosity profile. We then use an approximate relation between the viscosity profile and the ionic friction to determine conductivity. According to this treatment, when phrased in conventional terms, the effective Stokes radius of ions tends to be enhanced at low solvent densities so that a simple application of Stokes law with physical ionic radii and bulk viscosity is a gross overestimate of the contribution to conductivity. However, the decrease in solvent viscosity with decreasing density is such that the limiting equivalent conductivity is found to increase approximately linearly from subcritical through supercritical conditions, with no apparent plateau in low density SCW.

In order to test this result, we have also pursued a full dynamical simulation of ion diffusion coefficients in SCW. These simulations are computationally demanding, since relatively long runs are required to obtain statistically accurate results. Although these studies are not complete, the results for NaCl at a series of SCW densities (0.087g/cc - 0.5g/cc; 673K) show a remarkable feature. In all cases, the velocity correlation function, whose integral determines the diffusion rate, exhibits two time regimes. For very early times (< 0.5 ps), the frictional decay of the velocity is rapid and nearly constant with density for a given ion. However, there is a relatively slowly decaying tail in the velocity that is increasingly more distinct with decreasing density. This contribution would lead to increasing diffusion rates with decreasing density.

Planned Activities

The following planned activities will be performed in the last year. For the nitrogen oxide chemical equilibria, we are developing sophisticated optimization techniques to determine quantitative equilibrium constants for this complex reaction network. We also plan to study other equilibrium reactions with novel in-situ pH indicators developed in our laboratory for supercritical water.

On the theory side, we are now working on obtaining statistically precise results for the decays in the velocity correlation functions so that the behavior of conductivity with solvent density can be pinned down. It is also of considerable interest to determine the physical origin of the time scale that characterizes the slowest decay. One candidate is the dynamical time scale for sampling over alternative solvation structures in the solvated ion cluster, and we will also be pursuing an analysis of this hypothesis.

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Fundamental Chemistry and Thermodynamics of Hydrothermal Oxidation Processes

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Research Objective

The objective of this research program is to provide fundamental scientific information on the physical and chemical properties of solutes in aqueous solutions at high temperatures needed to assess and enhance the applicability of hydrothermal oxidation (HTO) to the remediation of DOE hazardous and mixed wastes. Potential limitations to the use of HTO technology include formation of deposits (scale) from precipitation of inorganic solutes in the waste, corrosion arising from formation of strong acids on oxidation of some organic compounds (e.g., chlorinated hydrocarbons), and unknown effects of fluid density and phase behavior at high temperatures. Focus areas for this project include measurements of the solubility and speciation of actinides and surrogates in model HTO process streams at high temperatures, and the experimental and theoretical development of equations of state for aqueous mixtures under HTO process conditions ranging above the critical temperature of water. A predictive level of understanding of the chemical and physical properties of HTO process streams is being developed through molecular-level simulations of aqueous solutions at high temperatures. Advances in fundamental understanding of phase behavior, density, and solute speciation at high temperatures and pressures contribute directly to the ultimate applicability of this process for the treatment of DOE hazardous and mixed wastes.

Research Progress and Implications

Research in this project has been divided into individual tasks, with each contributing to a unified understanding of HTO processing problems related to the treatment of DOE wastes. This report summarizes progress attained after slightly less than two years of this three-year project.

Fluid-Phase PVT Properties and Fluid+Fluid Phase Equilibria. Using a unique, custom-designed, high-pressure vibrating-tube densimeter, we are performing experiments to determine the densities and phase relations of O_2-N_2-CO_2-H_2O fluids at 523-773 K and 5-100 MPa. Data from these experiments are now being used to develop accurate new equations of state (EOSs) for H_2O-CO_2 fluids at 573, 623, and 673 K. The new EOSs are based on fitting "excess pressure" as a function of molar volume. This approach, which differs radically from the usual method of representing excess volume data for mixtures as a function of composition at constant temperature and pressure, allows us to build on the highly accurate equations of state for pure fluids which are currently available, taking advantage of the apparently simple dependence of the excess pressure on composition at constant molar volume of the mixture.

Solubility measurements. A method for determining solubility of solids in aqueous solutions as functions of temperature and pressure involving continuous monitoring of uranyl species in solution at high temperature by UV-visible spectrophotometry was developed in the first year of this program. Experiments on the solubility of uranium(VI) oxide conducted in a {carbonate + bicarbonate} aqueous buffer mixture indicated that the UO_3(cr) solid phase was not stable at temperatures above 373 K. In order to test whether the observed solubility behavior was due to the formation of uranyl carbonates,

additional solubility measurements were made on a uranyl carbonate solid. Characterization of the solid phase before and after high-temperature solubility measurements on $Na_4UO_2(CO_3)_3$(cr) clearly revealed two different solid phases, indicating that this solid is not stable at 393 K in equilibrium with the aqueous medium investigated. Solubility measurements at lower temperatures, where the solid is stable, showed a strong decrease in the solubility with increasing temperature.

Molecular Dynamics Simulation Studies of Aqueous Systems at High Temperatures. Our molecular-based investigation of high-temperature speciation (ion association and hydration) in dilute aqueous solutions has centered on molecular dynamics simulations of model NaCl(aq) solutions to study the behavior of relevant solvation properties within the first hydration shell of ionic species at supercritical conditions. More specifically, we determined the local-solvent density, local pressure, strength of the local electric field, and an estimate of the local dielectric constant along a near-critical isotherm and a supercritical isochore. The simulation work allowed us to characterized the solvent behavior in the vicinity of the ions in solution. There is a clear need for a rigorous formalism to relate macroscopic properties, which may diverge for dilute solutions near the solvent critical point, to the profound microstructural changes of the solvent around the ions and to the compressibility of the solvent. A new, unambiguous statistical mechanical formalism has been developed which details a clear-cut separation between the structural changes associated with the solvation of ions and the coexistent slow-decaying structural correlation.

Planned Activities

Multiple uranyl species are present in solid phases equilibrated with aqueous carbonate buffer solutions at elevated temperatures, and additional emphasis will be placed on characterization of post-experiment solid phases from future runs. Solubility measurements on UO_3(cr) will be extended to higher temperatures, using classical sampling and analysis techniques.

Additional measurements of the densities and phase relations of binary and ternary aqueous mixtures will include O_2 to give data needed to represent the behavior of HTO processes which include excess oxidizer. Further refinement and application of the newly developed representation for the volumetric properties of mixtures will continue as the experimental results are obtained.

Further simulation studies will use this formalism as a basis for the separation of solvation-driven and compressibility-driven contributions to macroscopic thermodynamic properties. Studies are being extended to include acidic (e.g., HCl) and basic (e.g., NaOH) solutes due to their central importance in corrosion of structural materials at high temperatures and pressures.

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New Anion-Exchange Resins for Improved Separations of Nuclear Materials

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Research Objective

The overall objective of our research is to develop a predictive capability which allows the facile design and implementation of multi-functionalized anion-exchange materials which selectively sorb metal complexes of interest from targeted process, waste, and environmental streams. The basic scientific issues addressed are actinide complex speciation along with modeling of the metal complex/functional-site interactions in order to determine optimal binding-site characteristics. Our new ion-exchange resins interface the rapidly developing field of ion-specific chelating ligands with robust, commercial ion-exchange technology. Various Focus Areas and Crosscutting Programs have described needs that would be favorably impacted by the new materials: Efficient Separations and Processing; Plutonium; Plumes; Mixed Waste; High-Level Tank Waste. Sites within the DOE complex which would benefit from the improved anion-exchange technology include Hanford, INEL, Los Alamos, Oak Ridge, and Savannah River.

Research Progress and Implications

As of April 1998, this report summarizes work after 1.6 years of a 3-year project. Our technical approach combines empirical testing with theoretical modeling (applied in an iterative mode) in order to determine optimal binding-site characteristics. We determine actinide-complex speciation in specific media, then develop models for the metal complex/functional-site interactions Synthesis and evaluation of multi-functionalized extractants and ion-exchange materials that implement key features of the optimized binding site provide feedback to the modeling and design activities. Resin materials which actively facilitate the uptake of actinide complexes from solution should display both improved selectivity and kinetic properties. Our implementation of the bifunctionality concept involves N-derivatization of pyridinium units from a base poly(4-vinylpyridine) resin with a second cationic site such that the two anion-exchange sites are linked by ‘spacer’ arms of varying length and flexibility.

Actinide-complex speciation: The primary actinides of interest in nitrate solutions are plutonium (IV) and americium (III). We have refined plutonium mono- and di-nitrato formation complexes. As expected, in higher ionic strength media, the formation of the tetranitrato complex shifts to lower acid concentrations than in pure nitric acid. Addition of a water-soluble anion-exchange polymer to solutions of plutonium in nitric acid also shifts the solution equilibrium to favor the dianionic hexanitrato complex, but with Kd values orders of magnitude lower than for the solid resins. Even americium(III), which does not form anionic nitrato complexes in pure nitric acid media, binds to the anion-exchange resins in solutions with excess nitrate. X-ray fluroescence experiments on Eu(III) (an Am surrogate) show that addition of excess nitrate results in the removal of one to two waters of hydration, but we have not been able to determine the exact anionic species. We have, however, begun pilot-scale evaluation of one new resin for the removal of Pu(IV) and Am(III) from process waste solutions.

Synthesis and evaluation of multi-functionalized extractants and ion-exchange materials: We have synthesized and tested a ‘systematic series’ of bifunctional resins that examines the effects of varying the following conditions:

1) The chemical structure of the second cationic site: pyridium > trimethylphosphonium > trimethylammonium.

2) The length and chemical structure of the spacer between the two cationic sites: generally a 4-5 atom spacer is optimal for plutonium uptake. A shorter spacer appears better for americium.
3) The percent crosslinking of the substrate: decreasing the crosslinking from 25% to 18% yields a ca. 50-100% increase in Kd with little impact upon resin stability.
4) The percent derivatization: performance increases with greater derivatization up to 100%. Most bifunctional resins, however, cannot be derivatized above 75%.

Two manuscripts (published, in press) and several presentations cover much of this work to date. We have synthesized and evaluated the first tri-functional (polystyrene-based) resin for plutonium/americium uptake. Preliminary tests of this particular material were disappointing in that, despite the higher cationic charge density, it did not display the Am(III) affinity that we had hoped for. We have completed synthesis, but not evaluation, of bifunctional extractants. We were able to achieve desired the organic miscibilibity for the dicationic material by adding two dodecyl groups to the pyridine functionality in the meta positions.

Modeling and design activities: We have developed partial charge and MM2 parameters for Pu, U, Th and Np (IV) nitrate systems. Using these parameters, we can very accurately model the nitrate-actinide interactions. Determination of the charge distribution of the hexanitrato dianions was problematic because of the exceptionally high orbital degeneracy of the complex. We developed a 'theoretical model' compound, the $Pu(NO_3)$ triradical, for which partial charges could be determined using ab initio calculations. Via calculation of the electrostatic interactions between the Pu-hexanitrato dianion and the dicationic "resin site", we have correlated the 'stickyness factor' with experimental Kds for three series of resins. Correlation is good using both formal charge and partial charge models. Two manuscripts (submitted, in preparation) cover this work to date. The models show that the butylene spacer for the trimethylammonium derivative of polyvinylpyridine changes from an 'anti' configuration in it's free state to a 'syn' configuration in the docked state. This observation has led to the hypothesis that a cis-butene spacer may exhibit improved sorption kinetics. We have synthesized, but not yet evaluated, a resin based on this functionality.

Planned Activities

Most of the baseline work was conducted on resins unsuitable for column applications, so we need to correlate those results with the new 21% cross-linked materials. We have begun extending this work to other actinide complexes (chloro-, carbonato-) and to non-actinide complex anions. Extension of the modeling activities to obtain predictive capabilities will require determination of the major energy terms which factor into the final Kd value. We hope to obtain this information via calorimetry and determination of Kd values for extractants and soluble polymeric forms. We would also like to extend our models to include the polymeric matrices and solvent effects. We anticipate completing the preliminary work in all these areas by the end of FY98/early FY99 and using the final year (FY99) to refine the work and develop applications.

Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO_2

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Dr. Mark A. Stadtherr, University of Notre Dame
John E. Chateauneuf, Western Michigan University

Research Objective

The overall objectives of this project are to gain a fundamental understanding of the solubility and stability of metal chelates in supercritical (SC) CO_2. Extraction with CO_2 is a excellent way to remove organic compounds from soils, sludges and aqueous solutions and recent research has demonstrated that together with chelating agents it is a viable way to remove metals, as well. We seek to gain fundamental knowledge that is vital to computing phase behavior, and modeling and designing processes using CO_2 to separate organics and metal compounds from DOE contaminated soils and mixed wastes. Our overall program is a comprehensive one to measure local solvation of metal chelates and to determine metal chelate stability in supercritical fluid (SCF) mixtures using UV-vis and FTIR spectroscopy. The spectroscopic studies provide information on the solution microstructure, which we are using in concert with our own and published solubility data to evaluate and develop thermodynamic models of the solubility behavior. Finally, we are implementing a more reliable computational technique, based on interval mathematics, to compute the phase equilibria using the thermodynamic models. This fundamental information about metal chelate stability and solubility in SC CO_2 is important in the design of processes using CO_2 to extract components from mixed wastes and in determining the optimum operating conditions.

Research Progress and Implications

This report summarizes work after 1 year and 8 months (9/15/96-5/14/98) of a 3 year project. Thus far, progress has been made in: 1) the measurement of the solubility of metal chelates in SC CO_2 with and without added cosolvents, 2) the spectroscopic determination of preferential solvation of metal chelates by cosolvents in SC CO_2 solutions, and 3) the development of a totally reliable computational technique for phase equilibrium computations.

1) An important factor in the removal of metals from solid matrices with CO_2/chelate mixtures is the equilibrium solubility of the metal chelate complex in the CO_2. While there are several researchers measuring the solubility of metal chelates in pure CO_2, we know of only one data point showing the influence of added cosolvents on solubility. Conversely, there are several reports that added methanol or the presence of water can significantly enhance extraction efficiencies. Therefore, we have measured the solubility of a simple b-diketonate complex, Zn(2,2,6,6-tetramethylheptane3,5-dionate)$_2$, at 40°C and 60°C in SC CO_2 and in SC CO_2 modified with 3 mole % methanol. At all conditions, the solubilities increase with increasing pressure and range between 0.002 and 0.005 mol/L in pure CO_2 at pressure between 2000 and 4000 psi. The addition of 3 mol % methanol results in an increase in the solubility of the metal chelate complex. At pressures from 2000 to 4000 psi the solubilities are 0.004 to 0.009 mol/L and 0.006 to 0.015 mol/L in 3 mol% methanol/CO_2 mixtures at 40°C and 60°C, respectively.
2) Based on literature results for polar organic solutes in SCF mixtures, an important contributor to the increased solubilities and increased extraction efficiencies of metal chelates in CO_2/cosolvent mixtures may be the preferential solvation of the metal chelate by the cosolvent. We have used UV-vis spectroscopy to measure the preferential solvation of Fe(acetylacetonate)$_3$ (Fe(acac)$_3$) by methanol in SC CO_2 at 40°C and 60°C. Initially, we had planned to measure

preferential solvation by solvatochromic shifts since there was a report of this method being used with $Fe(acac)_3$ in the literature (Tingey et al. *J. Phys. Chem*. 1989, *93*, 2140). Unfortunately, the UV-vis absorption peaks of $Fe(acac)_3$ do not shift with changing solvent environment. Fortunately, $Fe(acac)_3$ does show significant changes in the intensity of the metal to ligand charge transfer band ~431 nm, with higher intensities observed in nonpolar solvents. Thus, the ratio of the intensity of a more stable intraligand band ~272 nm to the intensity of the 431 nm band is a sensitive measure of the local environment around the metal chelate complex. We have used this technique to measure the preferential solvation of $Fe(acac)_3$ in SC CO_2/3 mole % methanol mixtures. The results indicate that the local environment around the $Fe(acac)_3$ is highly enriched with methanol (up to 16 times the bulk composition) and that it is largest at higher pressures. This is very different from trends observed for the preferential solvation of polar organic solutes in SCF. Careful examination of the spectra obtained revealed subtle changes in the spectra of $Fe(acac)_3$ in CO_2/methanol mixtures that are not present in either pure CO_2 or pure methanol, which may indicate specific chemical interactions. Nonetheless, the increases in local composition of the methanol around $Fe(acac)_3$ mirror the solubility enhancement and extraction efficiency increases observed when methanol is used as a cosolvent. Currently, we are using $Fe(acac)_3$ with other cosolvents. Small amounts of water in CO_2 causes dramatic changes in the intensity ratios in $Fe(acac)_3$, indicating a high degree of preferential solvation, as well as potential acid-assisted ligand exchange.

3) The purpose of solubility measurements and spectroscopic measurements of preferential solvation is the development of appropriate models of CO_2/ligand and CO_2/metal chelate complex phase behavior. Moreover, the reliable prediction of phase equilibrium from thermodynamic models is a key problem in the design and operation of processes using SC CO_2 to extract metals from contaminated soils and sludges. The solution of phase stability and, subsequently, phase equilibrium problems is well known to pose computational difficulties, as standard methods may converge to false or trivial solutions. In this project we are developing and applying a new method, based on interval mathematics, that is capable of solving the phase stability and equilibrium problems with mathematical and computational certainty that the correct result has been obtained. We have extended the applicability of the interval method to a wide variety of equation of state models, including the Peng-Robinson equation, that can be used to predict solubilities of chelating agents and metal chelate compounds in SC CO_2 and CO_2/cosolvent mixtures. Also, we have greatly enhanced the efficiency of the method by reducing or eliminating the overestimation of function ranges that are inherent in standard interval arithmetic. Thus far, our work has focused on the development of the general computational procedure.

Planned Activities

This report summarizes work after 1 year and 8 months (9/15/96-5/14/98) of a 3 year project. Thus far, progress has been made in 1) the measurement of the solubility of metal chelates in SC CO_2 with and without added cosolvents, 2) the spectroscopic determination of preferential solvation of metal chelates by cosolvents in SC CO_2 solutions, and 3) the development of a totally reliable computational technique for phase equilibrium computations.

1) An important factor in the removal of metals from solid matrices with CO_2/chelate mixtures is the equilibrium solubility of the metal chelate complex in the CO_2. While there are several researchers measuring the solubility of metal chelates in pure CO_2, we know of only one data point showing the influence of added cosolvents on solubility. Conversely, there are several reports that added methanol or the presence of water can significantly enhance extraction efficiencies. Therefore, we have measured the solubility of a simple b-diketonate complex, Zn(2,2,6,6-tetramethylheptane3,5-dionate)$_2$, at 40°C and 60°C in SC CO_2 and in SC CO_2 modified with 3 mole % methanol. At all conditions, the solubilities increase with increasing pressure and range between 0.002 and 0.005 mol/L in pure CO_2 at pressure between 2000 and 4000 psi. The addition of 3 mol % methanol results in an increase in the solubility of the metal

chelate complex. At pressures from 2000 to 4000 psi the solubilities are 0.004 to 0.009 mol/L and 0.006 to 0.015 mol/L in 3 mol% methanol/CO_2 mixtures at 40°C and 60°C, respectively.

2) Based on literature results for polar organic solutes in SCF mixtures, an important contributor to the increased solubilities and increased extraction efficiencies of metal chelates in CO_2/cosolvent mixtures may be the preferential solvation of the metal chelate by the cosolvent. We have used UV-vis spectroscopy to measure the preferential solvation of Fe(acetylacetonate)$_3$ (Fe(acac)$_3$) by methanol in SC CO_2 at 40°C and 60°C. Initially, we had planned to measure preferential solvation by solvatochromic shifts since there was a report of this method being used with Fe(acac)$_3$ in the literature (Tingey et al. *J. Phys. Chem*. 1989, *93*, 2140). Unfortunately, the UV-vis absorption peaks of Fe(acac)$_3$ do not shift with changing solvent environment. Fortunately, Fe(acac)$_3$ does show significant changes in the intensity of the metal to ligand charge transfer band ~431 nm, with higher intensities observed in nonpolar solvents. Thus, the ratio of the intensity of a more stable intraligand band ~272 nm to the intensity of the 431 nm band is a sensitive measure of the local environment around the metal chelate complex. We have used this technique to measure the preferential solvation of Fe(acac)$_3$ in SC CO_2/3 mole % methanol mixtures. The results indicate that the local environment around the Fe(acac)$_3$ is highly enriched with methanol (up to 16 times the bulk composition) and that it is largest at higher pressures. This is very different from trends observed for the preferential solvation of polar organic solutes in SCF. Careful examination of the spectra obtained revealed subtle changes in the spectra of Fe(acac)$_3$ in CO_2/methanol mixtures that are not present in either pure CO_2 or pure methanol, which may indicate specific chemical interactions. Nonetheless, the increases in local composition of the methanol around Fe(acac)$_3$ mirror the solubility enhancement and extraction efficiency increases observed when methanol is used as a cosolvent. Currently, we are using Fe(acac)$_3$ with other cosolvents. Small amounts of water in CO_2 causes dramatic changes in the intensity ratios in Fe(acac)$_3$, indicating a high degree of preferential solvation, as well as potential acid-assisted ligand exchange.

3) The purpose of solubility measurements and spectroscopic measurements of preferential solvation is the development of appropriate models of CO_2/ligand and CO_2/metal chelate complex phase behavior. Moreover, the reliable prediction of phase equilibrium from thermodynamic models is a key problem in the design and operation of processes using SC CO_2 to extract metals from contaminated soils and sludges. The solution of phase stability and, subsequently, phase equilibrium problems is well known to pose computational difficulties, as standard methods may converge to false or trivial solutions. In this project we are developing and applying a new method, based on interval mathematics, that is capable of solving the phase stability and equilibrium problems with mathematical and computational certainty that the correct result has been obtained. We have extended the applicability of the interval method to a wide variety of equation of state models, including the Peng-Robinson equation, that can be used to predict solubilities of chelating agents and metal chelate compounds in SC CO_2 and CO_2/cosolvent mixtures. Also, we have greatly enhanced the efficiency of the method by reducing or eliminating the overestimation of function ranges that are inherent in standard interval arithmetic. Thus far, our work has focused on the development of the general computational procedure.

Other Access To Information

A list of publications and presentations that are a result of this project will be available after 7/1/98 at: **http://www.nd.edu/~jfb/doeemsp/pubs.html.**

Managing Tight-binding Receptors for New Separations Technologies

Dr. Daryle H. Busch, University of Kansas

Dr. Richard S. Givens, University of Kansas

Research Objective

Whereas such traditional separation methodologies as ion exchange and solvent extraction require rapid interaction between ligands and metal ions, the most strongly binding ligands invariably bind slowly; e.g., cryptates bind and dissociate more slowly than macrocycles, which are slower than open-chain chelating ligands. This project seeks to maximize the binding and dissociation rates for tight-binding receptors in order to make them more useful to separations science. An alternative slow-binding technology is also under exploration.

Research Progress and Implications

Acceleration of Binding: Sixteen months into this 3 year project, seminal examples of a new class of ligands have been designed and synthesized, and the basic premise of the project has been confirmed. This work involves the design and synthesis of very special ligands that seek to capture the best properties of open-chain chelates and macrocycles. The ligands must begin as open-chain structures so they can bind fast, but they must have reactive groups that close the structures into macrocycles upon chelation to metal ions. There exists no literature precedent for such ligands, putatively because of the great tendency of the two ends of the molecule to react with each other. Synthetic challenges were indeed encountered en route to our first generation ligand **1**, a molecule in which the ligand extremities are carbonyl and amine groups that can condense to form a C=N linkage. The ligand has now been properly characterized and is available for detailed studies. Solution studies on the binding of ligand **2**, which is generated in solution, have confirmed the basic hypothesis that the rate of macrocyclic complex formation can be quite rapid when metal ion templated ring closure is involved. Solution studies have also shown that the Schiff base condensations like those involved in forming macrocyclic complexes with **1** and **2** can be reversed. Second generation ligands **3** and **4** are sought; the first to provide a macrocycle with no fused pyridine ring and the second to utilize a different ring closure reaction, ester exchange. **4** has been synthesized in high yield and characterized.

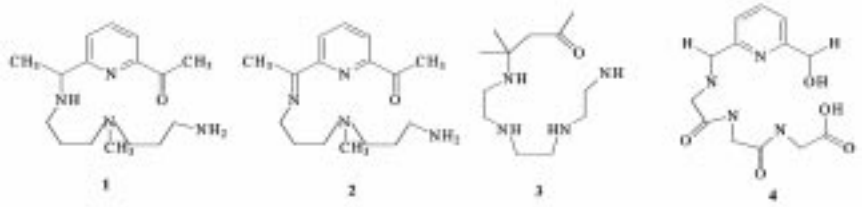

Figure 1

Planned Activities: Detailed equilibrium and kinetic studies of **1** will be conducted. Conditions for ring closure will be found for **4** and its derivatives. Synthesis of **3** will be completed. **3** and **4** will be subject to detailed study when appropriate. Third generation ligands will be designed and synthesized. Kinetic data will be compared with literature data on open-chain chelates and macrocycles.

A Biomimic as a Possible Slow Separations Technology: Certain single cell organisms secrete powerful sequestrants (siderophores) for iron and then absorb the iron complexes back through their membranes. Imprinted macroporous polymers[1] may provide the equivalent of the cellular membrane

for selective adsorption of complexes of tight-binding ligands. Separation by such a process need not be rapid and could exploit the full selectivity and strength of binding of the strongest ligands. N,N',N",N'"-tetrasubstituted 1,4,8,11-tetraazacyclotetradecanes (substituted cyclams) were investigated to test this concept. The substituents varied from those capable of covalent bonds (amines for Schiff base formation), good hydrogen bonders (amides) to moderate dipoles (nitriles). The mode of association also included incorporating anions (vinyl sulfonate) into the polymer. Complexes were incorporated into the matrix showing some promise, but work was discontinued to focus on other aspects of the project.

Photorelease of Metal Ions from Tightly Bound Adducts: Macrocycles capable of rapid release of tightly bound ions by photolytic fragmentation of the macrocyclic ring have been designed and are being synthesized. Two strategies for the synthesis of photolabile macrocycles have been pursued. In the first strategy, a substituted triazadioxo-15-crown-5 (**5**) has been synthesized by coupling 3-benzyloxy triethylene glycol ditosylate with a protected triazaundecane diol. This nine step synthesis to an intermediate macrocycle (see Appendix on web site) provides a general route to monosubstituted macrocycles. Conversion of the side chain into a photoactive ligand is in progress. Because of the lengthy procedure and low yields encountered using our earlier strategy, a second, more efficient synthesis for the substituted macrocycle was designed and carried out. In this second strategy (Appendix), the ring closure is accomplished by a Grubbs olefin metathesis using phenylmethylene bis(tricyclohexylphosphine)ruthenium dichloride. The 4-oxy-7,10,13-triazahexadeca-1,15-diene was closed to 2-hydroxymethyl-1-oxo- 4,8,12-triazatetradecane (**6**) in excellent yield (94%). Reduction of the double bond and hydrogenolysis of the protecting benzyl group has provided a much more efficient entry into an analogous hydroxymethyl substituted macrocycle which can be further elaborated into the photoactive macrocycle. Exploratory photochemistry of bis-7,16-(di-p-methoxybenzoyl)-1,4,10,13-tetraoxo-7,16- diazacyclooctadecane (**7**) has also been examined. No fragmentation of the crown ether was observed during irradiation either at 254 or 300 nm as anticipated for amides.

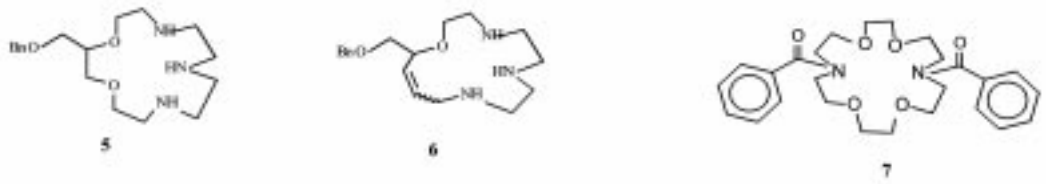

Figure 2

Planned Activities

Included above.

Extraction and Recovery of Mercury and Lead from Aqueous Waste Streams Using Redox-active Layered Metal Chalcogenides

Dr. Peter K. Dorhout, Colorado State University

Dr. Steven H. Strauss, Colorado State University

Research Objective

Mercury and other highly-toxic heavy metals such as cadmium and lead are present in many aquatic environments, and the remediation of such environments or the avoidance of heavy-metal contamination in the first place is an area of active interest. In recent years tougher environmental regulations and the high initial cost of new, more effective, and more selective extractants has made the reuse of extractant materials and the minimization of secondary waste volume a focus of our scientific effort. Our research has involved the investigation of redox-active layered metal chalcogenides as selective, effective, and redox-recyclable extractants for heavy metals from aqueous solution.

Research Progress and Implications

The use of lithium-intercalated transition-metal dichalcogenides, Li_xMS_2, as redox-recyclable ion-exchange materials for the extraction of the aqueous heavy-metal ions Hg^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} was investigated ($0.25 = x = 1.9$; M= Mo, W, Ti, Ta). For Li_xTiS_2 and Li_xTaS_2, hydrolysis produced $S^{2-}(aq)$ ions which precipitated Hg(II) as HgS(*s*). In contrast, the materials Li_xMoS_2 and Li_xWS_2 did not undergo hydrolysis to form S^{2-} ions. Instead, ion-exchanged materials such as $Hg_{0.50}MoS_2$ and $Pb_{0.15}MoS_2$ were isolated. The selectivity of Li_xMoS_2 for the heavy-metal ions was $Hg^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+}$. The affinities for the latter three ions, but not for Hg^{2+}, increased when the extractions were performed under anaerobic conditions. When Hg_yMoS_2 was heated under vacuum at 425°C, an entropy-driven internal redox reaction resulted in deactivation of the extractant, producing essentially mercury-free MoS_2 and a near-quantitative amount of mercury vapor (collected in a cold trap). The ratio of the volume of metallic mercury (secondary waste) to the volume of 10.0 mM $Hg^{2+}(aq)$ (primary waste) was 1.5×10^{-4}. Samples of MoS_2 produced by heating Hg_yMoS_2 were reactivated to Li_xMoS_2 by treatment with *n*-butyllithium. Some samples were used for three cycles of extraction, deactivation/recovery, and reactivation with a primary waste simulant consisting of 10 mM $Hg^{2+}(aq)$ in 0.1 M HNO_3 with no loss in ion-exchange capacity. When the Mo/Hg molar ratio was 5.0 and the initial $[Hg^{2+}(aq)] = 1$ mM, only 0.033(2) μM mercury (6.5 ppb) was detected in the filtrate after the extraction step. The highest observed capacity of Li_xMoS_2 for $Hg^{2+}(aq)$ was 580 mg mercury per g $Li_{1.9}MoS_2$. Initial experiments have indicated that Li_xWS_2 is also a redox-recyclable extractant for $Hg^{2+}(aq)$.

Since two of the lithium-intercalated transition metal dichalcogenides, Li_xMoS_2 and Li_xWS_2, investigated showed promise as effective, selective, and redox-recyclable extractants for heavy metal ions from aqueous solution we decided to study of the mechanisms of activation, extraction, deactivation, and recovery of the extractant and the target ion. This investigation has involved the use of powder X-ray diffraction (XRD), differential scanning calorimetry (DSC), and X-ray absorption spectroscopy (XAS). Based on our results, we believe that heavy-metal ions are removed from solution by a reversible ion-exchange process with the negatively charged metal chalcogenide layers. The extracted heavy-metal ions are present in the interlayer space of the layered solid-state extractant. We have also determined that the metal ions are present, in the heavy-metal-loaded extractant, in a sulfur rich coordination environment and that the heavy-metal ions are in an oxidized form. The

XAS investigation indicated that the selectivity of the extractants may be based on the ability of certain heavy-metal ions to stabilize the negatively charged (reduced) metal-chalcogenide layers (that have a distorted geometry relative to the neutral (oxidized) metal-chalcogenide layer). The stabilization ability of the metal ions appears to correlate strongly with their degree of soft-Lewis acid character. The softer Lewis acids, such as Hg^{2+} and Ag^{+}, are very effective at stabilizing the reduced chalcogen layers and are hence removed to a large extent. However, metal ions such as Ni^{2+}, Zn^{2+}, and Mn^{2+}, that are harder Lewis acids than Hg^{2+} and Ag^{+}, are not as effective at stabilizing the reduced chalcogen layers and hence are removed to a far lesser extent than both Hg^{2+} and Ag^{+}.

Planned Activities

We are actively investigating both the optimization of the Li_xMoS_2 and Li_xWS_2 extractants and the development of new redox-active layered extractants. Both the Li_xMoS_2 and Li_xWS_2 extractants do generate some hydrogen gas during the extraction process. Naturally, we would like to eliminate this potentially dangerous side product and are currently synthesizing Li_xMoS_2 and Li_xWS_2 extractants that will generate no hydrogen and are still effective extractants. We have shown that Li_xMoS_2 is an effective, selective, and redox-recyclable extractant for $Hg^{2+}(aq)$ through at least three complete cycles of activation/extraction and reactivation/recovery. We would like to study both of the Li_xMoS_2 and Li_xWS_2 extractants through many more cycles of activation/extraction and reactivation/recovery. We are also interested in studying the feasibility of using electroactive conducting polymer films containing MoS_2 and WS_2 particles for effective, selective, and redox-recyclable extraction of heavy-metal ions from aqueous solution.

There are new alkali-metal-intercalated metal chalcogenides that remain to be investigated. Three such materials that will be studied are the lithium-intercalated SnS_2, VS_2, and $NiPS_3$ compounds. All of these materials have been synthesized previously as Li_xMS_2 or Li_xMPS_3 and will be tested by the methods we have developed for our Li_xMS_2 (M = Mo, W, Ti, Ta) studies.

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Web Access

http://www.chm.colostate.edu/

De Novo Design of Ligands for Metal Separation

Dr. Garland R. Marshall, Washington University

Research Objective

Develop computer-aided molecular design technology for ligands useful in metal separations. This includes force field parameterization of different metals in various oxidation states and de novo design of ligands optimized for specific metals including constriants to certain chemical classes of ligands.

Research Progress and Implications

This report summarizes year two of a 3-year project and focuses on force field parameterization.

Work continues on the modification of algorithms to construct metal-binding ligands from molecular fragments. The lack of an appropriate theoretically derived functional form for d-orbitals in molecular mechanics has hampered efforts to utilize these programs and our efforts have focused on correcting this deficiency in collaboration with Prof. Anders Carlsson of the Department of Physics as follows:

Our approach for parametrization of transition metal atoms is to fit an empirical potential for molecular mechanics to the potential energy surface calculated by ab initio methods. Conventional ab initio methods1 using Hartree-Fock theory are known to give good results for most organic molecules. Coordination compounds require the use of high-level basis functions such as triple zeta valence (TZV) to get accurate results which are highly time consuming thus restricting the ligand sizes. In order to overcome these difficulties, the density functional model2-4, which is known to give results in parallel to the popular MP2 model was used.

The d-electron energy function plays an important role in transition metal complexes. Recently, an energy function for d-electrons has been derived at Washington University based on quantum mechanical analysis.5 The d-shell energetics is described via the 'ligand field stabilization energy', which is given by

E LFSE = - [Â e(ri) e(rj) U(qij)] (1)
ij

e(ri) , e(rj) are the coupling strengths of the individual ligands and the qij is the ligand-metal-ligand angle. U(qij) is an angular function defined as,

U(qij) = [P (cos qij)2 -(1/5)] ,

where P = (3 cos2 q - 1) / 2.

The functional forms of the coupling strengths can be derived from the half-width, W, of the d-complex. The term W is related to the energies of the occupied and the empty d-orbitals by the following term;

_
5W2 = Â (Œn-Œ)2
n _

Œn is the energy of the occupied d orbitals and Œ is the average energy of the occupied and unoccupied d orbitals.

In order to derive the functional form of W and coupling strengths, ab initio and density functional calculations were performed on various metal complexes. We have initially studied square planar and tetrahedral metal ammonia (Mn^{+2},Fe^{+2},Co^{+2},Ni^{+2},Cu^{+2},Zn^{+2}) and copper-imidazole complexes. Geometry optimizations were performed at UHF for open shell systems and RHF for closed shell systems, using triple zeta valence (TZV) basis set in ab initio and BP/DN* in density functional model. Optimized geometries for the Cu^{+2}-imidazole complex shows good agreement with known crystal structures.

The variation of half width with respect to metal ligand distance was then computed by varying the metal-ligand distances. Detailed studies have been carried out for Cu-ammonia and Cu-imidazole complexes. The exponantial functional form of the coupling strength was then derived from least squares fit and the value of W(*) was optimized so that the sum of the squares of the error is minimum around the equilibrium distance. The following function is obtained from the least squares fit;

W(r) = W(*) + b e -a r

W(r) is the half width at a particular metal-ligand distance r.

The best least squares fit gave a value of 0.035 Hartrees for W(*), the coefficient b is 0.19378 Hartrees and the exponent is 1.79108 Å-1 for the Cu-ammonia and Cu-imidazole complexes. Further studies for various other combinations of metals and ligands are underway. Some of our preliminary studies have shown that the parameter W varies not only with the metal-ligand distance, but also with the varying ligands.

The importance of the angular term in the equation (1) can be understood by comparing the energetics of the square planar vs the tetrahedral geometries. The computed energy differences for the square vs tetrahedral complexes show the magnitude of angular term changes and hence the preference for a particular geometry which varies depending on the central metal atom.

Planned Activities

It is our intent to validate the force field parameters for various metals of interest by modeling a variety of known complexes which were not used in parameter development. These parameters will then be included in the TINKER modeling package which is available over the internet. They will also be incorporated into our de novo design software and ligands designed to be selective for various metals of interest. This will be accomplished in the remaining year of the project.

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Removal of Heavy Metals and Organic Contaminants from Aqueous Streams by Novel Filtration Methods

Dr. Nelly M. Rodriguez, Northeastern University

Research Objective

Graphite nanofibers are a new type of material consisting of nanosized graphite platelets where only edges are exposed. Taking advantage of this unique configuration our objective is:

- To produce graphite nanofibers with structural properties suitable for the removal of contaminants from water.
- To test the suitability of the material in the removal of organic from aqueous solutions.
- To determine the ability of the nanofibers to function as an electrochemical separation medium the selective removal of metal contaminants from solutions.

Research Progress and Implications

This report summarizes work after 1.5 of a 3-year project. During this period, efforts have been concentrated on the production, characterization and optimization of graphite nanofibers (GNF). This novel material has been developed in our laboratory from the metal catalyzed decomposition of certain hydrocarbons (1). The structures possess a cross-sectional area that varies between 5 to 100 nm and have lengths ranging from 5 to 100 mm (2). High-resolution transmission electron microscopy studies have revealed that the nanofibers consist of extremely well-ordered graphite platelets, which are oriented in various directions with respect to the fiber axis (3). The arrangement of the graphene

layers can be tailored to a desired geometry by choice of the correct catalyst system and reaction conditions, and it is therefore possible to generate structures where the layers are stacked in a "ribbon", "herring-bone", or "stacked" orientation. The research has been directed on two fronts: (a) the use of the material for the removal of organic contaminants, and (b) taking advantage of the high electrical conductivity as well as high surface area of the material to use it as electrode for the electrochemical removal of metal pollutants from aqueous streams.

(a) Use of GNF in the Removal of Organic Contaminants from Water.
In the first part of this project the suitability of graphite nanofibers for the adsorption of selected organic molecules from aqueous solutions was tested by allowing a solution of a given organic to interact with selected samples of GNF. In a typical experiment, 0.2 g of the carbonaceous solid was placed in a solution containing 0.5 mL of a ethyl or butyl alcohol in 60 mL of deionized water. The material was continuously stirred and maintained at room temperature for up to 160 hours. Care was taken to prevent loss of the alcohol due to evaporation by keeping the container covered. The uptake of alcohol by the carbon was monitored as a function of time by taking samples of the solution at various periods of time that were analyzed by Gas Chromatography. Identical experiments were conducted using an active carbon sample possessing a surface area ~ 7.5 times that measured for GNF.

Carbon nanofibers possessing a high degree of crystalline order have been found to exhibit excellent adsorption characteristics for the removal of small amounts of alcohol from aqueous solution. A comparison with active carbon shows that even though the nanofibers have a surface area that is 7 times lower their performance for this separation process is far superior to that displayed by the former material. A further feature to emerge from this work is the finding that pre-treatment conditions have a critical impact on the subsequent adsorption behavior; while prolonged immersion in hydrochloric was found to be extremely beneficial, a similar treatment in nitric acid virtually nullified the advantages of using nanofibers for the process.

(b) Use Of GNF for the Extraction of Metallic Contaminants from Aqueous Streams
The potential of GNF for the removal of metals from aqueous solutions was tested in a specially built plug flow cell, which consists of two chambers filled with the carbon material. Details of the design of the cell are well documented in the literature (4,5). In this arrangement, nanofibers in one of the chambers function as the cathode, whereas the material placed in the second compartment acts as the anode. A saturated calomel electrode was used as reference. Water is purified by flowing a solution through the cell where the metal ions are removed from solution via an electrochemical reduction process that occurs on the nanofibers present in the cathode. Once the nanofibers are saturated with the metal, the contaminant can be collected in conjunction with the carbonaceous material or, if desired, discharged into a more concentrated solution by switching the voltage. This process allows for both the purification of water as well as the recovery of the metal in a higher concentration for further application. These experiments were performed by applying a potential to the cell, which is controlled by a CMS300 PC3 potentiostat. Concentration of ions were determined by an induced coupled argon plasma (Leeman Plasma-Spec).

Preliminary work indicates that when a 170 ppm copper sulfate in 0.0166 M sulfuric acid solution (ion source) is passed over a 2.0 gram GNF bed, 2 cm in length, then up to 97% of the copper content is eliminated from the solution at a -8.5 V.

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Planned Activities

- We plan to use GNF for the removal of a variety of organic contaminants from aqueous solution and at the same time, develop methods for the recovery of these chemicals.
- In a complementary series of experiments efforts will be focused on the examination of various nanofiber surface treatments in an attempt to enhance their adsorption capacity.
- An investigation of the adsorption efficiency of GNF as a function of increasing the surface area of the material from 50 to 600 will be carried out.
- The effect on adsorption characteristics of organics resulting from an expansion of the GNF lattice via insertion of selected groups within the layers will be conducted.
- Finally, we shall explore the impact of increasing the degree of crystallinity of the GNF on the use of the material as an electrode in electrochemical devices.

Rational Synthesis of Imprinted Organofunctional Sol-Gel Materials for Toxic Metal Separation

Dr. Ziling (Ben) Xue, University of Tennessee

Sheng Dai, Oak Ridge National Laboratory
Craig E. Barnes, University of Tennessee

Research Objective

The objective of this program is to rationally design and synthesize imprinted sol-gel SiO_2 and SiO_2/$M'O_2$ (M' = Ti, Zr) materials containing Si-X-L binding groups through template approaches and develop a scientific basis for metal ion binding and recognition by such imprinted organofunctional materials. These hydrophilic metal oxide-based materials are expected to remove metal ions from aqueous solutions intrinsically fast (in comparison to hydrophobic organic polymers), and the imprinted binding sites are expected to exhibit enhanced selectivity and affinity of target metal ions.

Research Progress and Implications

This report summarizes research after the first eight months of a three-year project. We have successfully prepared sol-gel materials grafted with organic ligands specific for binding target RCRA metal ions. When these organofunctional sol-gel materials are exposed to solutions containing target metal ions, they quickly remove the metal ions from aqueous solutions. In many such sol-gel materials, the metal ions absorbed in the sol-gel materials can be easily removed to regenerate the organofunctional sol-gel materials for subsequent cycles of metal ion removal.

Work has commenced in two main areas: (1) preliminary evaluation of target ion binding and imprinting effects, (2) studies of mesoporous materials for the separation of large metal ions such as UO_2^{2+} and TcO_4 .

Preliminary Evaluation of Target Ion Binding and Imprinting Effects

We have conducted studies to evaluate (a) the removal of target metal ions from aqueous solutions by organofunctional sol-gel materials containing grafted ligands; (b) the recovery of the metal and regeneration of the organofunctional sol-gels. The target metal ions in the preliminary evaluation are Cu^{2+}, Hg^{2+}, Sr^{2+} and UO_2^{2+}.

Cu^{2+}, Hg^{2+} and Sr^{2+} Binding Studies. These three ions are among the regulated RCRA metal ions. Ethylene diamine linked to -$Si(OMe)_3$ (N-N) was the principal reagent used in these studies. The sol-gels were prepared by first reacting the N-N ligand with M^{2+} to form a complex $M(N\text{-}N)_n^{2+}$. The complex is then mixed with a cross-linking reagent $Si(OMe)_4$ and water to give the imprinted sol-gels. Another approach is to directly mix the N-N ligand with $Si(OMe)_4$ and water without a metal template to prepare the non-imprinted sol-gels. We have improved the sol-gel formation process to give more robust materials.

Preliminary data show that metal uptake capacities of these N-N grafted sol-gels are 0.15-0.35 mmol/g for Cu^{2+}, 1.0 mmol/g for Hg^{2+} and 0.3-0.4 mmol/g for Sr^{2+}. Adding acid (HCl) readily protonates the N–N ligands and strips M^{2+} from the sol-gels. After neutralizing, the gel is again capable of removing M^{2+} from aqueous solutions. This cycle can be repeated many times. Preliminary data demonstrated that imprinted sol-gels had a higher capacity for binding Sr^{2+}.

UO_2^{2+} Binding Studies. Organofunctional silica sol-gels (imprinted and non-imprinted with UO_2^{2+}) have been prepared and their uptake of uranyl measured. Imprinting is shown to enhance the UO_2^{2+} uptake in diethylmalonate grafted sol-gels. The non-imprinted sol-gels have an affinity for uranyl (0.03 mmol/g) similar to that of SiO_2. The imprinted samples exhibited a significantly higher affinity (0.12 mmol/g). Several silicate sol-gels grafted with other ligands (phosphonate esters, propyl amine, ethylene diamine, cyanopropyl and mercaptopropyl) have also been tested for uranyl uptake. In addition, TiO_2 and mixed SiO_2/TiO_2 sol-gels were studied. The uranyl affinity for a series of mixed SiO_2/TiO_2 sol-gels with varying Si : Ti ratios was found to increase with the amount of titanium in the sample.

Synthesis of Mesoporous Materials

Mesoporosity is critical to the performance of a sol-gel sorbent in removing metal ions such as UO_2^{2+} and TcO_4 from solution. Our research showed that the kinetics of uranyl binding by sol-gels was strongly linked to the mesoporosity of the materials. Although frequently exhibiting high total surface areas, samples that are predominately microporous bind uranyl significantly more slowly than samples that are predominantly mesoporous. Two approaches for preparing mesoporous sol-gels have been successfully developed.

Surfactant Templated Mesoporous Organofunctionalized Sol-Gels. The use of surfactants in sol-gel synthesis is known to produce mesoporous materials. The effect of surfactant templates such as cetyltrimethylammonium bromide and dodecylamine on the pore structure of organofunctional as well as SiO_2/TiO_2 mixed sol-gels has been studied. In the sol-gels grafted with phosphonate, amine or ethylenediamine, predominantly mesoporous materials were prepared (d = 20 - 25 ; surface area = 700 - 1000 m^2/g) which rapidly bound UO_2^{2+} from aqueous solution. Mesoporous mixed SiO_2/TiO_2 sol-gels which are stable to alkaline conditions were also prepared using dodecylamine as the template (d = 31 ; surface area = 760 m^2/g).

Prehydrolysis. Prehydrolysis of sol-gel precursors was investigated to inhibit the formation of microporous organofunctional sol-gels without the use of surfactants. Prehydrolysis of mixtures of $(EtO)_4Si$ and $(EtO)_3Si$(vinyl) under acidic conditions followed by neutralization was found to give mesoporous materials (d = 36 ; surface area = 700 m^2/g). Mesoporous (d = 40 - 200) materials with surface areas between 100-300 m^2/g were also obtained by prehydrolyzing $(EtO)_4Si$ and the alkylammonium salt $(MeO)_3Si(CH_2)_3NMe_3Cl$ before gellation at neutral pH.

Our research and the preliminary results in the past eight months demonstrate that the sol-gels grafted with metal-specific ligands are potentially good sorbents for metal separation. These results have laid a solid foundation for the research in the remaining period of this project.

Planned Activities

In the next 12 months, in addition to confirming the earlier preliminary results, we will focus our attention on the capacity and selectivity of the imprinted ligand-grafted sol-gels. We will also explore grafting to sol-gels new ligands with known high affinity for target metals, and study the separation

of other RCRA metals by our novel imprinted organofunctional sol-gel materials. In the final year of this project, we plan to conduct simulated waste tests involving these sol-gel materials, and optimize the overall process.

Real-Time Broad Spectrum Characterization of Hazardous Waste by Membrane Introduction Mass Spectrometry

Dr. Philip H. Hemberger, Los Alamos National Laboratory

Mary Cisper, Los Alamos National Laboratory

Research Objective

The objective of this project is to expand the capabilities of Membrane Introduction Mass Spectrometry (MIMS) to the pivotal problem of Mixed Hazardous Wastes, with secondary emphasis on monitoring incinerator stack gases for both organics and toxic metals. The methodologies developed in this proposal could also be applied to other environmental monitoring problems that require highly sensitive on-line detection of volatile and semi-volatile organic compounds, and heavy metals

Research Progress and Implications

As of May 1, 1998, we have designed and tested the rare gas ionization source and the associated ion optics. Ions are generated in a microwave plasma which can be supported by helium or argon from room air. A series of extraction and focusing lenses followed by a linear quadrupole serves to inject ions into the ion trap. Injection efficiency and favorable trapping of externally-generated ions are dependent on several parameters including lens potentials, quadrupole operation, buffer gas pressure, kinetic energy of the injected ions, and amplitude of the trapping potential. We have investigated rf-only operation of the linear quadrupole. RF/DC operation will be studied as a means for further reducing interferences. A publication on this work has been submitted to Int. J. Mass. Spectrom. Ion Proc.

To date we have used MIMS to detect 40 volatile and SVOCs without preconcentration, primarily from an air matrix. The 40 analytes range in boiling point from 21 to 279° C and include chlorinated and oxygenated solvents, chlorophenols, polyaromatic hydrocarbons, and substituted benzenes.

Using MIMS, we have demonstrated the direct, simultaneous detection of a volatile organic compound, a semi-volatile organic compound, and an organometallic compound with a single analytical technique in near real-time for two waste streams, air and water. To our knowledge, this is the first time this has been accomplished.

We have investigated the analysis of several organometallic compounds containing heavy metals by MIMS. These include lead and tin compounds. When these molecules are analyzed, organic fragment ions are observed. However, neither the intact molecular ion, nor the metal ion species are seen in the mass spectrum. These results are interesting because in the spectra of metal compounds most of the ion current is normally carried by metal-containing species [J. Charalambous, ed., Mass Spectrometry of Metal Compounds].

We speculate that it is oxygen, present either as a neutral or as an ionized species, that may be inhibiting the appearance of metal-containing fragment ions in certain cases. Oxygen is one of the predominating species in the ion trap environment in our experiment. Its high availability for secondary reactions as either a neutral or positively charged ion and the stability of possible products from these

secondary processes may make the detection of metal-containing ions problematic in the current set-up. The formation of highly refractory neutral metal oxides, for example, would preclude the detection of metal-containing fragment ions.

We are investigating experimental means to test the questions that have been raised by these observations. Other ion trap instruments in our lab with additional capabilities to study ion/molecule chemistry may provide help in testing and resolving this issue.

Various researchers have investigated in situ ethylation using the reagent sodium tetraethylborate for the determination of heavy metals in environmental samples. In aqueous solution, sodium tetraethylborate will ethylate ionic lead, tin, and mercury species to produce volatile derivatives. We have reviewed the pertinent literature and are preparing a study incorporating MIMS and in situ ethylation of tin compounds, a number of which are toxic to marine life.

Planned Activities

For the remainder of FY98 we will focus on the detection of organic compounds using membrane introduction combined with the microwave source/ion trap mass spectrometer. In FY99, we will continue to focus on semi-volatile organic compounds and their ion chemistry in discharge ion sources, and in parallel, we will extend our preliminary investigations of MIMS of metal-containing compounds.

Other Access To Information

Although the following two papers appeared in print before this proposal was funded, they provide an introduction to the MIMS methodology and show its potential for the characterization of semi-volatile organic compounds and metals:

M.E. Cisper, P.H. Hemberger, Rapid Commun. in Mass Spectrom., 1997, 11, 1449.
M.E. Cisper, P.H. Hemberger, Rapid Commun. in Mass Spectrom., 1997, 11, 1454.

A publication arising from this work has been submitted. This paper describes the application of a combined microwave plasma source/ion trap mass spectrometer for atmospheric analysis of fixed gases and volatile organic compounds.

Genetic Engineering of a Radiation-Resistant Bacterium for Biodegradation of Mixed Wastes

Dr. Mary E. Lidstrom, University of Washington

Research Objective

Because of their tolerance to very high levels of ionizing radiation, members of the genus Deinococcus have received considerable attention over the past years. The type species of the genus, Deinococcus radiodurans, has been studied extensively in several labs. Although researchers are only beginning to understand the mechanisms by which this Gram-positive bacterium is able to repair massive DNA damage after radiation dosages as high as 5 Mrad, it has become evident that its recombination machinery has several unique characteristics (1-4).

The aim of the present studies is to engineer D. radiodurans into a detoxifier for bioremediation of complex waste mixtures, containing heavy metals, halo-organics and radionuclides, making use of its ability to be biologically active in environments where they will be exposed to high levels of

radiation. For that purpose, we aim to clone and express several broad spectrum oxygenases and heavy metal resistance determinants, and test survival and activities of these strains in artificial mixtures of contaminants, designed to simulate DOE mixed waste streams.

1) Daly, M.J., et al. (1996) An alternative pathway of recombination of chromosomal fragments precedes recA-dependent recombination in the radioresistant bacterium Deinococcus radiodurans. J Bacteriol 178: 4461-4471
2) Daly, M.J., and Minton, K.W. (1995) Resistance to radiation. Science 270: 1318
3) Minton, K.W., and Daly M.J. (1995) A model for repair of radiation-induced DNA double-strand breaks in the extreme radiophile Deinococcus radiodurans. Bioessays 17: 457-464
4) Battista, J.R. (1997) Against all odds: The survival strategies of Deinococcus radiodurans. Annu Rev Microbiol. 51: 203-224

Research Progress and Implications

Progress Report

This report summarizes work after 0.5 year of a 3-year project. The initial studies have focused on the development of an insertional expression system for D. radiodurans R1. This effort has involved two parts, namely: (1) promoter analysis, and (2) development of insertion systems.

Several studies have shown that the expression signals used by D. radiodurans differ considerably from those found in other bacteria. Although D. radiodurans contains a typical eubacterial RNA polymerase core enzyme (based on TBLASTN searches on the genome sequence), Escherichia coli promoters are not recognized in D. radiodurans and vice versa (5). To expand our basic understanding of the requirements for transcription, and to optimize expression of (heterologous) genes, we will follow two strategies. First, a promoter-probe vector is being developed for the selection of promoter sequences from the D. radiodurans R1 genome. This system, which uses either lacZ or gfp as a reporter for expression, is based on single-copy replacement recombination (DCO) in either the thyA or dfrA (folA) gene. From numerous studies in both Gram-positive and Gram-negative organisms it is known that mutations in these genes, encoding thymidilate synthase and dihydrofolate reductase, respectively, render the host resistant to trimethoprim (e.g., 6). This obviates the need of an efficiently expressed antibiotic resistance marker for the initial selection of transformants. This system will then be used for the construction of a shotgun-library of promoter fragments and subsequent screening of D. radiodurans transformants for expression of b-galactosidase or fluorescence. The second strategy involves primer extension studies of a number of genes which are expected to be transcribed at a substantial level. This will enable us to map transcription start sites and identify possible -35 and -10 sequences.

Two potential integration systems have been developed, one based on insertion into amyE (a-amylase), and a second based on insertion into amyX (pullulanase) genes. A kanamycine-resistance marker has been used to test both systems and both appear to be good candidates for an insertion vector. In both cases, double cross-over recombinants were obtained that showed both kanamycin-resistance and loss of function, i.e. failure to grow on the appropriate substrate as sole carbon and energy source (starch or pullulan).

5) Smith, M.D., et al. (1991) Gene expression in Deinococcus radiodurans. Gene 98:45-52
6) Stacey, K.A., and Simson, E. (1965) Improved method for the isolation of thymine-requiring mutants of Escherichia coli. J Bacteriol 90: 554-555

Planned Activities

In the next 6-12 months we will characterize promoters, generate an expression system for the insertion vector, and optimize expression of cloned broad-range oxygenases.

Hazardous Gas Production by Alpha Particles in Solid Organic Transuranic Waste Matrices

Dr. Jay A. LaVerne, University of Notre Dame

Research Objective

This project uses fundamental radiation chemical techniques to elucidate the basic processes occurring in the heavy-ion radiolysis of solid hydrocarbon matrices such as polymers and organic resins that are associated with many of the transuranic waste deposits or the transportation of these radionuclides. The environmental management of mixed waste containing transuranic radionuclides is difficult because these nuclides are alpha particle emitters and the energy deposited by the alpha particles causes chemical transformations in the matrices accompanying the waste. Most radiolysis programs focus on conventional radiation such as gamma rays, but the chemical changes induced by alpha particles and other heavy ions are typically very different and product yields can vary by more than an order of magnitude. The objective of this research is to measure the production of gases, especially molecular hydrogen, produced in the proton, helium ion, and carbon ion radiolysis of selected solid organic matrices in order to obtain fundamental mechanistic information on the radiolytic decomposition of these materials. This knowledge can also be used to directly give reasonable estimates of explosive or flammability hazards in the storage or transport of transuranic wastes in order to enhance the safety of DOE sites.

Research Progress and Implications

This report summarizes the work after eight months of a three-year project on determining the production of hazardous gases in transuranic waste. The first stage of the project was to design and build an assembly to irradiate solid organic matrices using accelerated ion beams. It is necessary to measure absolute radiolytic yields, and simulate some of the conditions found in the field. A window assembly was constructed allowing the beam to pass consecutively through a collimator, a vacuum exit window and into the solid sample. The beam is stopped in the sample and the entire end of the assembly is a Faraday cup. Integration of the collected current, in conjunction with particle energy and charge, allows for accurate determination of dose. A stream of gas, such as nitrogen, flows between the sample and the beam exit window to flush away gaseous products that evolve from the sample surface. The gas steam is sampled with a quadrupole mass spectrometer. By monitoring the desired mass peak with the spectrometer it is possible to quantitatively determine a number of different products on line.

The first experiments have focused on the hydrogen evolution in polyethylene irradiated with protons and helium ions. Hydrogen is the main gaseous product formed and there have been some previous studies using gamma rays (1) and low energy (<= 1 MeV) H, He, B, and Ar ions (2). The yield of hydrogen was found to decrease from 0.67 molecules/100 eV energy absorbed with 5 MeV protons to 0.11 with protons of 15 MeV. The protons have a linear energy transfer, LET, of 21 to 10 eV/nm, respectively. Hydrogen yields should increase as the LET increases, but the absolute yields are lower than expected suggesting that other processes are involved in its formation or evolution from the bulk.

Literature values for hydrogen production in gamma radiolysis range from 2.4 to 2.7 molecules/ 100 eV (1), which compares well with our value of 2.7. Previous studies with low energy particles also suggest hydrogen radiation chemical yields of 1 to 3. Further studies with gamma radiolysis have shown that with thick samples of polyethylene a considerable fraction of the hydrogen can be retained in the sample in spite of the large diffusion coefficient (> 10-7 cm2/s) of hydrogen in solid polymers (3). It appears that the retention of gases in heavy ion irradiated material is larger than that found in gamma radiolysis. The reason for this outcome is unknown. Such a large capture of hydrogen

in the bulk can have a large consequence of the management of waste material and will be studied thoroughly.

1. H. Mitsui and Y. Shimizu J. Polym. Sci. 1979, 17, 2805.
2. M. B. Lewis, E.H. Lee, L.K. Mansur, and W.A. Coghlan J. Nucl. Mater. 1994, 208, 61.
3. T. Venkatesan, W.L. Brown, C.A. Murray, K.J. Marcantonio, and B.J. Wilkens Polym. Engin. Sci., 1983, 23, 931.

Planned Activities

A series of experiments to be performed in the next few months will examine the formation and evolution of hydrogen in thin samples. The information obtained will help determine true hydrogen production yields. Other studies varying sample thickness will help determine hydrogen diffusion and retention in bulk materials. A model of hydrogen diffusion and/or percolation in the bulk from ion tracks will be developed to aid in data interpretation. Different organic matrices, such as polystyrene and various resins, will be examined because of their fundamental and practical importance. Hydrogen production will also be examined under different atmospheric conditions. Oxygen or water vapor instead of nitrogen will simulate more realistic conditions and give fundamental information on possible surface effects on hydrogen formation.

An apparatus for the next generation of experiments is currently being designed and constructed. These experiments will enable the analysis of gaseous products produced form solid matrices in ultra high vacuum. Under these conditions, a number of different products with relatively small yields can be measured simultaneously and correlation made between their yields and incident particle characteristics such as charge, energy, and LET. In the next year, an attempt will be made to examine the bulk material following irradiation. A significant increase in crosslinking is expected. This information will give more understanding of the radiolytic processes involved and enable better prediction of outcomes in systems that are not possible to be examined experimentally.

The Sonophysics and Sonochemistry of Liquid Waste Quantification and Remediation

Dr. Thomas J. Matula, University of Washington

Research Objective

To perform an in-depth and comprehensive study of the fundamentals of acoustic cavitation and nonlinear bubble dynamics, to elucidate the fundamental physics of sonochemical reactions, to examine the potential of sonoluminescence to quantify and to monitor the presence of alkali metals and other elements in waste liquids, to design and to evaluate more effective sonochemical reactors for waste remediation, and to determine the optimal acoustical parameters in the use of sonochemistry for liquid-waste-contaminant remediation.

Research Progress and Implications

This report summarizes work performed during year 2 of a 3-year project. Our goals included performing near-IR spectroscopy of sonoluminescence. Cells have been designed for multi-bubble sonoluminescence (MBSL) and single-bubble sonoluminescence (SBSL) spectroscopy experiments.

The MBSL cells are designed around a 20 kHz acoustic horn with replaceable titanium tips from Sonics & Materials. The horn is pressure-fitted into a stainless steel cell via O-rings and a compression ring, to seal the cell up to 100 psi for pressure experiments. The cell is thermostated by circulating coolant in a jacket, as well as flowing the cell fluid (at 4L/min.) through a temperature control bath. Several ports are located on the cell for gas ports (one for headspace, another for bubbling), a pressure transducer, a thermocouple, a needle hydrophone, and a septum port for addition or withdrawal of samples. The total volume is approximately 80 mL with a 10 mL head space. Directly opposite the horn tip is a 2 cm quartz window against which a fiber optic bundle is placed. Light collected through the fiber optic is imaged onto one of several detection systems.

SBSL cells were designed to provide maximum light throughput, since it was expected the near-IR intensities would be extremely low. We utilized a 45 mm diameter levitation cell, with a PZT transducer glued to the bottom of the cell. Fluid ports with leak-proof detachable connectors allowed for replacing the dissolved air with other gases. A photomultiplier tube (PMT) was used to record the overall light intensity, and to monitor the bubble stability. A computer-controlled system was used to generate a bubble, if the previous bubble became unstable, or disappeared. Initial experiments utilized a lens system to focus the emitted light onto the fiber optic bundle. This arrangement is acceptable, since the wavelength range that was studied was relatively narrow.

Positive results were obtained in both systems during year-2 using a Raman system, on loan from Kaiser Optical, Inc. This instrument covers the wavelength range from 790 to 1070 nm. Both single bubble and multiple bubble sonoluminescence spectra have been taken over this range, using air/water, argon/water, and argon/NaCl-water solutions. The intensities of both MBSL and SBSL decline towards the red end of the spectra for all systems studied. A dip in intensity from 960 to 1020 nm is observed in the single bubble spectra. This is probably due to the water absorption band in the near-IR. The dip is not apparent in the multiple bubble system, where cavitation occurs adjacent to the observation port (the path length through water is small). The profiles are otherwise quite similar for air/water and argon/water, with no spectral features, suggesting similar mechanisms for the observed light emission. The sodium doublet near 818/819 nm was observed in the MBSL system with a concentration as low as 0.5 molar. The lower concentration limit for detection of this doublet has not yet been explored. Sonoluminescence spectra from this wavelength region have never before been reported.

Further progress from year-1 involved the use of the newly discovered technique of changing the pressure head above the cavitation field to increase the light emission from MBSL. As the static pressure was slowly increased from atmospheric pressure (760 mmHg) to 4 atmospheres (3040 mmHg), the sonoluminescence intensity increased to a global maximum around 3.3 atmospheres (about 2480 mmHg) in our system, at which point the intensity began to decrease again. In year-2, we found that with pure water, no hysteresis was observed during this static pressure variation. However, if a sodium solution is used instead of pure water, a great deal of hysteresis around the intensity maximum occurs. One possible mechanism for the hysteresis involves the sodium acting to shield individual bubbles so that, once created, they are prevented from coalescing. To be useful in quantitative studies, the concentration would have to be much lower than used in these initial experiments (1 molar). Further studies are now being conducted to determine the lower concentration threshold for hysteresis effects. Additionally, this maximization of the sonoluminescence intensity may be useful for minimizing power consumption for economical alkali waste monitoring.

A second method for changing the pressure head involves pressure-jumping, whereby the pressure in the head space above the solution is quickly increased to a new steady value. This pressure-jump results in a dramatic increase in the light intensity that can last minutes. In order to obtain a better understanding of the physical processes occurring in the multiple bubble acoustic cell, the fiber optic was replaced with an endoscope to visually observe the bubble field (in absence of data collection). During a pressure jump experiment, the cloud of cavitation bubbles at atmospheric pressure disappears from sight at the moment of increasing the pressure to 3.3 atmospheres. As cavitation continues, microscopic bubbles are seen to grow in size. The time with which it takes the bubbles to grow to pre-pressure jump sizes corresponds with the end of enhanced emission when the light intensity is measured. These results agree with the new notion that small bubbles are responsible for the sonoluminescence emissions, and presumably, for sonochemical activity.

Planned Activities

We plan to use spectroscopic studies to determine if our pressure-jumping results in "hotter" bubbles, or simply more bubbles of the same temperature. We have also begun experiments to determine the feasibility of finding mercury emission lines from sonoluminescence. These experiments should last for approximately 3 months. These studies are designed to determine whether or not MBSL can be used to quantify mercury contaminants in waste pump oil. We have also undertaken a study to determine the mechanism for intensity quenching of sonoluminescence with alcohols, and other organics. As outlined in the original proposal, these studies will last for approximately 11 months.

Other Access To Information

The results of our research have been published in scientific journals, and presented at scientific meetings. A list of published papers and conference presentations is presented below:

A. Brodsky, "Casimir free energy of a spherical cavity in a dielectric medium," J. Mathematical Physics, 38, 5127-5142 (1997).

D. Kuhns, A. Brodsky, and L. Burgess, "Hydrodynamical perturbation effects in multiple bubble sonoluminescence," Phys. Rev. E, 57, 1702-1704 (1998).

T.J. Matula and L.A. Crum, "Evidence for gas exchange in Single-bubble sonoluminescence," Physical Review Letters, 80, 865-868 (1998).

T.J. Matula, "Sonoluminescence," European Society of Sonochemistry, Plenary lecture, May, 1998

T. Matula, "Sonoluminescence: Some recent results," NATO Advanced Study Institute, invited lecture, September, 1997.

Adsorption/Membrane Filtration as a Contaminant Concentration and Separation Process for Mixed Wastes and Tank Wastes

Dr. Mark M. Benjamin, University of Washington

Gregory Korshin, University of Washington

Research Objective

Separate Sr and Cs from other constituents Hanford tank wastes (Na, Al, NO_3, Ca) in a form that allows them to be further processed and, ultimately, disposed of appropriately.

Research Progress and Implications

This report describes progress through May, 1998, which is a little past mid-way through the second year of a three-year project. The goal of the research is to develop a treatment system for the separation of contaminants in low-organic Hanford tank wastes into various sub-groups that are relatively easy to treat further to yield products that are amenable to final disposal. The main target contaminants are Sr and Cs, although heavy metals and actinide-group elements are also targets.

Effort during the first half-year of the project was devoted primarily to development of experimental and analytical techniques that could be used to test and quantify the treatability of Sr and Cs in the extremely complex matrix of the tank wastes. The treatment technologies to be tested for isolation of

Sr from other waste constituents included adsorption of Sr onto various mineral solids and membrane separation of particulate from dissolved Sr. The proposed technology for treating Cs was electrochemically controlled, reversible binding of the Cs to hexacyanoferrates. Results obtained during the remainder of the first year suggested that hematite (a-Fe_2O_3) and iron-oxide-coated sand (IOCS) were the best adsorbents for Sr among the oxides tested, and work during the second project year followed up on that result.

Sr adsorption from simulated tank solutions containing ~3 M $NaNO_3$, ~2 M NaOH, ~0.5 M $Al(NO_3)^3$, 3 x 10^{-5} M $Sr(NO_3)^2$, and 0.11 M $Ca(NO_3)^2$ was evaluated in systems containing hematite. The hematite (with the adsorbed Sr) and any other solids were then separated from the solution using ultrafiltration or microfiltration membranes. When the hematite was dosed at a concentration of 100 mg Fe/L in batch systems, nearly 100% of the Sr adsorbed onto the hematite. However, when this Sr:Fe ratio was scaled up and used in a continuous flow system using ultrafiltration for solid/liquid separation, Sr removal from solution was near 100% for only a short time before the removal efficiency began to decline. Over the course of two hours, the water flux through the membrane decreased from ~165 to ~150 L/m^2-hr, and Sr removal declined from ~100% to ~40%.

The results for treatment using IOCS were much more favorable. The simulated waste has been treated by passage through three columns in series, using a 5-min empty bed contact time in each column. A fourth column was prepared as well, and the system has been run continuously for 38 days in an arrangement where three columns are in use and the fourth is being regenerated at any given time. To date, the Sr concentration in the final effluent (from the third column in the series) has been undetectable. Each column has been regenerated (using a solution at pH 3) five times, with no apparent deterioration in performance. We propose to continue using this system for Sr treatment, exploring the effects of competing metal ions and organic complexing agents, over the next several months.

The separation of cesium from simulated Hanford waste (SHW) was pursued using an electrochemically controlled system built around an electrode modified with Co(II) hexacyanoferrate. The active phase in this electrode is Men[CoFe(CN)6], where Me is a mono- or di-valent cation that is reversibly exchangeable for cesium. The oxidation state of the iron is controlled electrochemically by an external potentiostat. The active phase was formed by direct contact between Co(II) and hexacyanoferrate ions in the host electrode. Theoretically, the amount of cesium that can be retained by the electrode is controlled by the amount of the active phase and the oxidation state of the hexacyanoferrate iron. The reduction of Fe(III) to Fe(II) in a Cs-containing solution perturbs the charge balance of the hexacyanoferrate matrix and initiates the influx of Cs ions whose summary charge restores the electroneutrality. When the Fe(II) is electrochemically oxidized to Fe(III) in a regenerating solution, the cesium is expelled from the hexacyanoferrate matrix, and the electrode's capacity to bind Cs is restored. In theory, these cycles can be repeated indefinitely.

To study the performance of the cesium-active electrodes, three types of experiments have been conducted. First, the reactions of several non-electrochemically controlled cesium-active hexacyanoferrates (Fe, Co, Cu, Zn, Ni, Cd) were examined at varying pHs, ionic strengths, reaction times. Cobalt hexacyanoferrate was found to be superior to others in terms of pH stability and selectivity to cesium. The kinetics of incorporation of cesium into the active matrix depended to some extent on the preparation technique (e.g., freeze-drying, thermal treatment); this issue will be studied in more detail in the coming year. The pH stability of hexacyanoferrates at pH greater than 11 or 12 might be a fundamental limitation of their applicability of this approach for treating highly basic Hanford wastes without adjusting their pH.

In the second group experiments, the electrochemistry of hexacyanoferrate-modified graphite electrodes was studied. Activation substantially increased the current through the electrode. The typical peaks associated with the incorporation/ expulsion of counter-cations were observed and quantified.

In the third group of experiments, the charge passed through the electrode in solutions containing from $<10^{-5}$ to $>10^{-2}$ M cesium was measured chronoamperometrically and compared with the amount of cesium released in a regenerating solution. The amount of cesium taken up by the electrode was from 50 to 120% of the total charge associated with the oxidation/ reduction of the iron. Sodium in the concentration range up to 5 M did not interfere with the performance of the electrode.

The focus of current and planned experiments is on the stability of the modified electrodes at high pH, kinetics of cesium incorporation and release, effects of mass transfer to the electrode surface, the reuse of the regenerating solutions, and effects of interfering species on the electrode surface and the active phase. Ways to increase the amount of the active phase in the electrode, accelerate the kinetics of its reactions with cations and improve the electrochemical control are being investigated.

Planned Activities

Sr removal by IOCS will be investigated as a function of the concentration of Ca, heavy metals, and organic complexing agents. The regenerability of the IOCS over many regeneration cycles will be explored, and the possibility of reusing the regenerant solution will be explored, so that the volume of regenerant requiring further processing will be minimized. These tasks will be carried out simultaneously over the next six to eight months.

Cs removal by reversible incorporation into Co hexacyanoferrates will be explored further, with a focus on the kinetics of mass transfer and Cs binding and release, the reversibility of the binding over many cycles, and the effects of potentially competing ions. These studies will be carried out in parallel over the next nine months.

Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance

Dr. Kristin Bowman-James, University of Kansas

George S. Wilson, University of Kansas
Krzysztof Kuczera, University of Kansas
Bruce Moyer, Oak Ridge National Laboratory

Research Objective

This project has as its focus the design and synthesis of polyammonium macrocyclic receptors for oxoanions of environmental importance. The basic research aspects of this project involve: (1) synthesis (and the search for improved synthetic methods); (2) solid state structure determination and thermodynamics studies (to ascertain structural criteria for and strength of anion binding); and (3) molecular dynamics simulations (to assess solution characteristics of the interactions between anions and their receptors). Applications-oriented goals include the fabrication of more selective anion-selective electrodes and the use of these compounds in liquid-liquid separations. The latter goal comprises the subcontract with Dr. Bruce Moyer at Oak Ridge National Laboratory.

Research Progress and Implications

This report summarizes work after 1 year and 7 months of a 3-year project. To date, we have focussed on the design and synthesis of selective receptors for nitrate and phosphate.

Synthesis. The synthesis of polyaza macrocycles, which are the focus of these studies, is in many cases tedious and time-consuming. For example, the synthesis of **1** can take as long as one month because of purifications required during the synthetic route. A major breakthrough in year one of the project was to identify other polyaza macrocycles which bind the desired anions, but which are simpler to synthesize via two step Schiff base/reduction processes with high yields. This is truly significant since now we can obtain large quantities of the macrocycles and can do a variety of

studies at the same time. During year one most of our studies focused on monocyclic systems containing two diethylenetriamine units separated by spacers, **2 - 6**. In year two (as a result of findings from molecular dynamics simulations), we began to examine bicyclic macrocycles, **7 - 11**, which can be synthesized by the same method starting with the tetraamine known as *tren*.

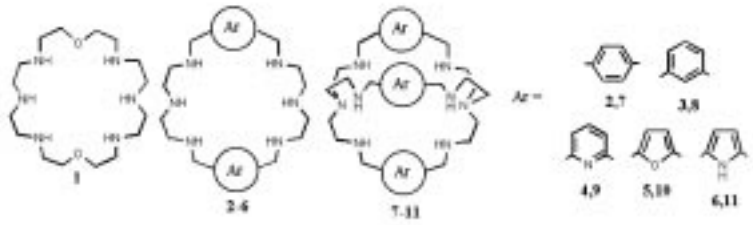

Figure 1

This year we have also have begun the exploration of the synthesis of receptors which have "switching" capabilities, including redox switches (disulfide [oxidized form] and sulfhydryl [reduced form]) and photochemical switches (azobenzenes). This work is currently in progress.

Structural studies. (1) *Anions*. We now have eleven crystal structures of nitrate complexes with polyaza macrocycles, seven with monocycles and four with bicycles. We have one monocycle structure with phosphoric acid/dihydrogen phosphate. The latter is unique in that phosphoric acid is actually part of the structure.

The very recent (March 1998) isolation and structural characterization of a bicycle, **8**, with threefold symmetry containing two encapsulated nitrate ions is our most significant finding, which impacts the existing base of knowledge concerning anion receptors. Two nitrates were found to crystallize inside the macrocyclic cavity in an eclipsed conformation, separated by only 3.33 Å. In addition to being the first instance of nitrate bound within a receptor cavity, this is the first example of a receptor incorporating two discrete anions within a single cavity. This finding is truly significant since all anion binding studies to date assume that a only one discrete anion will be bound within a cavity. We now have strong evidence, including NMR, potentiometric titration, and x-ray crystallographic, that this is not necessarily the case. This exciting result indicates that these C_3 bicycles hold considerable promise as receptors for trigonal anions, and furthermore that we are not limited to just one anion for incorporation into the cavity. We also have evidence that the furan analog (**10**) incorporates nitrate within the cavity, but the structure appears to be disordered and we are still working on it.

(2) *Schiff base macrocycles*. We have completed structures of some of the anion free macromonocycles formed by the initial condensation of dien with dialdehydes. These interesting structures shed light on mechanistic considerations involved in the Schiff base condensations.

(3) *Switches.* We have obtained a crystal structure of a prototype disulfide switch macrocycle.

Molecular dynamics (MD) studies. Simulations on several complexes using the program CHARMM indicate that hydration effects tend to govern the structure of the receptor in solution so that it becomes relatively planar even if the solid state structure indicates a folded conformation. Also all of the dihedral angles NCCN tend to adopt the *trans* configuration (*ca.* 180° C), which tends to minimize the repulsive electrostatic interactions between the positively charged amino groups. MD studies have also indicated that in solution water plays an important role in forming relay networks to the macrocycle from surrounding nitrates. The results of the theoretical computations pointing to a preference for planarity in monocycles led us to explore bicyclic compounds, which would presumably be forced to maintain a relatively spherical shape in solution. As noted above, this led to the isolation and structural characterization of the encapsulated dinitrate complex.

Potentiometric studies. Protonation constants are being determined for each of the macrocycles, and binding constants are being determined for selected anionic substrates. An important experimental finding was that the use of the hexahydrochloride salt in these studies was not recommended, as complex formation tends to influence the pK_as as well as subsequent binding constants for nitrate.

Hence, the *p*-toluenesulfonate macrocyclic salts were obtained assuming that the large counterion would be more "benign", and data were considerably improved and are very reproducible. The results of the potentiometric studies indicate that for monocycles, association constants are disappointingly low (*ca*. 10-100), undoubtedly due to the interfering or competing influence of hydration as noted in the MD studies. However, affinities of the bicyclic receptors for nitrate are considerably larger (*ca*. 10^{3-5}). We have just completed the binding studies with the bicycle **8**, and the potentiometric curves show the formation of both the mono-nitrate and di-nitrate complexes (log $[LH_6(NO_3)]/[LH_6][NO_3]$ = 2.94(8) and log $[LH_6(NO_3)_2]/[LH_6][NO_3]^2$ = 5.70(8)) at pHs up to 6. (Our studies with monocycles indicate that these receptors only form complexes with nitrate at pHs less than 4.)

Electrode studies. A comprehensive study on optimizing the conditions for the electrode films has just been completed. These studies are considerably more difficult than for analogous cation selective electrodes because of tricky solubility problems. Findings indicate that 1,2-dimethyl-3-nitrobenzene and 2-fluorophenyl-2-nitrophenyl ether are improved plasticizers over 1-decanol. Preliminary studies using the bicyclic macrocycles as ionophores have just commenced and initial findings indicate promising selectivities for nitrate, but not yet at the level of the commercially available electrodes.

Planned Activities

Oak Ridge. Separations studies. (Subcontract with Bruce Moyer at Oak Ridge National Laboratory) Studies at Oak Ridge will begin this summer now that several promising receptors have been identified. One of my postdoctoral associates will go to Oak Ridge for these studies. Since these studies were delayed the first year, there will be considerable interaction with the Oak Ridge group in probing the utility of these complexes in separations technology in the coming year.

University of Kansas. We will continue to investigate multiple binding and incorporation of anions within bicycle cavities. As part of this study we will also probe the chemistry, i.e., because of the short N—N separation for the two nitrates, they may be activated chemically. New amide based receptors, designed along the same lines as the bicyclic polyamines, are being synthesized and will be tested in the separations studies this summer. It is desirable to obtain receptors which are active at higher pHs (for radioactive waste remediation), and amides may meet this goal. Continuing efforts in the design and synthesis of switches are ongoing and will be accelerated when a new postdoctoral associate arrives next month. In the next and last year of the project, we will explore receptor design for the other oxoanions that were targeted in the proposal as well as for photo- and redox-activated switches. We will continue in applications oriented studies including separations and ion selective electrodes.

Other Access To Information

Book

Supramolecular Chemistry of Anions, Bianchi, A.; Bowman-James, K.; García-España, E.Wiley-VCH: New York; 1997, 461 pp. (ISBN 0-471-19622-8). This is the first comprehensive text reviewing the current state-of-the-art in anion chemistry.

Publications

Papoyan, G.; Gu, K.; Wiorkiewicz-Kuczera, J.; Kuczera, K.; Bowman-James, K., Molecular Dynamics Simulations of Nitrate Complexes with Polyammonium Macrocycles: Insight on Phosphoryl Transfer Catalysis Crystal Structure of a Nitrate Inclusion Complex, *J. Am. Chem. Soc.* 1996, *118*, 1354-1364.

Mason, S.; Clifford, T.; Seib, L.; Kuczera, K.; Bowman-James, K., Unusual Encapsulation of Two Nitrates in a Single Bicyclic Cage, under revision as a communication in *J. Am. Chem. Soc*.

Wiórkiewicz-Kuczera, J.; Kuczera, K.; Bazzicalupi, C.; Bencine, A.; Valtancoli, B.; Bianchi, A; Bowman-James, K., Solution and Solid State: Molecular Dynamics Simulations and Crystal Structure of the Nitrate Salt of an Octaazamacrocycle, to submitted to *J. Am. Chem. Soc*.

Web site

The structure of the bicycle with two nitrates may be viewed at the following web site: **http://129.237.102.17/~kuczera/kristin/animate.html.**

Novel Miniature Spectrometer for Remote Chemical Detection

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Research Objective

This research will develop an entirely new class of chemical sensing technology that will enable qualitative and quantitative remote, real-time optical diagnostics of chemical species in hazardous gas, liquid, and semi-solid phases through a completely novel implementation of evanescent wave spectroscopy. The sensor design uses a tiny, solid block (< $1cm^3$) of ultra-high purity optical material that is fabricated into a regular, planar polygon with a convex facet to form a total-internal-reflection ring cavity. Cavity ring-down detection measures the absorption of evanescent waves by chemical species in contact with the cavity. By interfacing the cavity to a remotely located light source and detection system (e.g., 0.1 to 10 Km away), this new technology will permit remote, high-sensitivity, broadband chemical sensing with a rugged, cost-effective, miniature spectrometer.

Research Progress and Implications

This report summarizes work conducted after 1 year of a 3-year project. In brief, the laboratory program demonstrated the operation and sensitivity for chemical detection of a prototypic, square total-internal-reflection (TIR) minicavity ringdown spectrometer. We confirmed experimentally the theoretical predictions of performance and refined strategies for cleaning the surfaces and for practical, integrated packaging of the TIR spectrometer with its coupling optics. In addition, a simple, solid-state, TIR, non-ring resonator cavity was designed which may speed practical implementation of this technology for EMSP applications. This design is outlined in the propriety section of this report.

The experimental program utilized a prototype square miniature spectrometer comprised of a 7.5x7.5 mm block of high-purity fused silica and two coupling prisms. To form a stable TIR ring cavity, one face of the block is convex. Extremely high reflectivity (~99.9999%) is achieved by superpolishing each face to a surface roughness of ~ 0.05 nm. One fused silica prism is placed close to one facet to inject laser light into the cavity and a second prism extracts a small fraction of the circulating light and transmits it to a photodetector. The coupling efficiency and cavity performance are functions of the alignment and spacing of these coupling prisms. Hence, much time was invested to determine the alignment and gap width that optimizes the spectrometer performance. In the test stand of the prototype, the alignment and gap widths of the coupling prisms were adjusted with piezoelectric driven translation stages and goniometers. To prevent system drift, an active stabilization system used interferometry and Newton's rings to measure and stabilize the gap-widths of the coupling prisms. Extensive experiments have verified that the optimum gap between the minicavity and each prism is 2-3 micrometers when the spectrometer is operated between 520 and 680 nm. These experiments will facilitate the design of integrated modules that use fixed and adjustable gaps.

A series of experiments were conducted that verify the performance of this spectrometer against the predictions of advanced modeling calculations. These calculations predicted that this minicavity should exhibit a characteristic ring-down time of 1.8 microseconds at 620 nm. Indeed, this decay time was experimentally observed by using a commercial 8-bit, 1-Ghz digital oscilloscope. This corresponds to a cavity loss of 50 parts-per-million-per-pass, which yields practical detection sensitivity for absorbance changes of 0.1 parts-per-million.

Experiments have demonstrated that the square cavity is very sensitive to chemical species that adsorb onto a fused silica face. Iodine was selected for these experiments because it has a quantitatively characterized optical spectrum and their vapor pressure and saturation densities upon glasses have been measured previously. During these experiments a cell containing iodine was placed against one facet and the time-dependent extinction of the evanescent wave was monitored

as the surface coverage by iodine increased. Measurements were performed between 520 and 680 nm. The measurements showed that the square resonator could detect iodine surface coverage of 0.001 monolayer! Further optimization may yield one to two orders of magnitude increase in sensitivity.

Several minicavities for use in aqueous solution were also explored with advanced computational modeling. The most sensitive design for use in the visible spectrum is octagonal minicavity fabricated from fused silica. Designs based upon other substrates were investigated of which the most intriguing is composed of high quality sapphire. Sapphire should produce very rugged devices that can operate in the very useful fingerprint near-IR and mid-IR spectral regions. Because sapphire has a relatively high refractive index, the critical angle for TIR in aqueous media is reduced and the minicavity geometry is a cheaper-to-produce, hexagonal solid.

Planned Activities

Experiments that measure the sensitivity of the square cavity design for chemical species deposited from vapors will continue. When the prototypes of a new, simplified resonator design (discussed in the proprietary section of this report) are delivered, their performance properties will be characterized. Strategies for fiber-optic coupling of these cavities to lasers and detectors also will be investigated.

A sapphire hexagonal minicavity prototype will be fabricated to permit measurements of solution-phase anions and metal cations. Time permitting, we will also integrate this resonator with an infrared laser source and perform measurements of solution-phase species in the near- and mid-IR spectrum. During the next year we hope to develop interactions with EMSP technical personnel who can help us select realistic performance tests so that interest in field deployment is stimulated.

Other Access To Information

The technical progress of this project is reported at http://www.nist.gov/crds. As appropriate, rigorously detailed descriptions of this work are published in the scientific journals and patent literature. Two patents related to this technology are pending. Two publications on this technology are available in the archival literature:

1) "Evanescent Wave Cavity Ring-down Spectroscopy as a Probe of Surface Processes", A.C.R. Pipino, J.W. Hudgens and R.E. Huie, Chem. Phys. Lett. 280, 104 (1997).
2) "Evanescent Wave Cavity Ring-down Spectroscopy with a Total-internal-reflection Minicavity", A.C.R. Pipino, J.W. Hudgens and R.E. Huie, Rev. Sci. Instrum. 68, 2978 (1997).

The Development of Cavity Ringdown Spectroscopy as a Sensitive Continuous Emission Monitor for Metals

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Christopher B. Winstead, Mississippi State University

Research Objective

A critical need exists for the development of methods to monitor toxic metal concentrations in remediation system offgases in real-time at parts-per-billion levels or lower. Although several technology development projects are being pursued to meet the requirements of a multi-element metals continuous emission monitor (CEM), no current technique has met all the requirements of sensitivity and data quality. The use of cavity ringdown spectroscopy (CRS) as an ultra-sensitive

analytical technique is a natural extension of previous atomic absorption spectroscopy methods. However, while CRS has rapidly gained popularity among the molecular spectroscopy community, the work reported here concerns the first efforts to apply this technique to analytical atomic spectroscopy. The objective of this project is to combine CRS with the well-established tools for sample atomization, the inductively coupled plasma (ICP) and graphite furnace (GF), to provide a viable technique for on-line, trace level continuous emission monitoring of species such as toxic metals and radionuclides with detection limits comparable to ICP-mass spectroscopy (ICP-MS).

Research Progress and Implications

This report summarizes our progress in the first year of a 3-year project to develop cavity ringdown spectroscopy as a sensitive, continuous emission monitor for metals. Progress has been slightly delayed by problems associated with freeing up the matching funds necessary to purchase a new narrow-linewidth dye laser and the typical problems encountered when departments move into a new building. However, these problems have been largely solved. Our new laser system has recently arrived and additional matching funds have been obtained for the purchase of a graphite furnace. This instrument is on order and will arrive in the near future. The postdoctoral and graduate positions have been filled.

Before discussing our achievements to date, a brief outline of the technique will be useful. In a typical cavity ringdown experiment, a laser pulse is injected into a stable optical cavity formed from two highly reflective dielectric mirrors and is trapped between the mirror surfaces. The light stored in the cavity decays exponentially with a time constant determined by the mirror reflectivity and the sample concentration within the cavity. The decay time is measured using a photomultiplier tube and fitted to a single exponential function which, in turn, yields the sample concentration. For the highest reflectivity mirrors available, a pulse circulating in the cavity can result in kilometers of effective pathlength. To perform elemental analysis using CRS, an atomization source (e.g. ICP & GF) is required (see ref. 1 & refs. therein).

Initial experiments have focused on ICP-CRS using a 1.6 kW, 27.12 MHz argon ICP (standard Fassel torch) equipped with an ultrasonic nebulizer. A frequency doubled Nd:YAG laser pumped tunable dye laser with pulse duration of approximately 10 ns and repetition rate of 10 Hz. The resulting laser output is of the order of 0.3 cm^{-1} linewidth. This is approximately twice the linewidth of the absorption feature, implying that the apparent absorption linewidth is a combination of both the actual absorption and the laser linewidth. As with standard absorption spectroscopy[4], CRS absorbance measurements require the use of a linewidth narrower than the absorption line. Thus these initial results suffer from a reduced sensitivity since a significant fraction of the pulse energy remains in the cavity even after light in resonance with the atomic transition has been absorbed. This problem is eliminated with the use of the new laser system.

Various radius of curvature mirrors, coated for different wavelength ranges, have been tested for cavity construction and stability. The interface between the ICP and optical cavity systems has also been investigated especially with regard to the baseline time constant stability. The cavity has been designed and tested to minimize the fluctuations caused by the introduction of the ICP into the cavity. The stability of the technique has been studied using two very different cavity configurations. Short cavities (56 cm long) were constructed from 0.5 and 5 meter radius of curvature mirrors. Both near confocal (0.5 m) and near planar (5 m) cavity geometries were tested during ICP operation and yielded a standard deviation in baseline (no analyte) ringdown times of approximately 1%. Results obtained both with and without the ICP plasma indicate that while the ICP does not appear to have severe effects on the measured time constant stability, it does slightly reduce the magnitude of the time constant. This implies additional losses in the ICP other than absorption by analyte atoms. Research is currently underway to explain this observation. The effect of spatial filtering and mode matching optical configurations on the input laser pulse have also been evaluated.

Our trace species investigations have focused, to this point, on the detection of Pb using ICP-CRS (although we have also observed Mg and OH, Fig. 7 in Ref. 1 depicts the relative absorbance measured as the laser is tuned across the 283.3 nm Pb absorption line). The initial goal in the operation of an ICP-CRS system is the production of primarily ground state analyte atoms (i.e., similar to ICP-AFS). Full optimization, however, requires consideration of the influence of ICP

torch design and operation, observation height within the ICP, gases and gas flow for the ICP torch, wavelength selection, and calibration procedures. Additional important considerations are interference effects, light scatter, sample transport, matrix effects, and spectral interferences.

With the introduction of analyte into the ICP, the ringdown time clearly drops as the solution concentration increases. However, a deviation from linearity is observed at high concentrations. While such effects are common in traditional atomic absorption spectroscopy, an additional component leading to non-linearity in our data is the linewidth of the laser. Research4 has found an ~8 times improvement in ringdown response with a reduction to a narrow linewidth. At lower concentrations, an excellent linear response is obtained. Our preliminary results with the old laser system indicate a ppb detection limit for Pb. While this value is still one to two orders of magnitude from theoretical values for ICP-CRS, the new laser has yet to be incorporated and significant work on system optimization remains to be completed. These early results place ICP-CRS among the most sensitive of optical analysis methods for ICPs. Continued improvements are expected, with a complete multi-parameter optimization strategy to be implemented in the future. These improvements should make ICP-CRS a viable alternative to ICP-MS in many analytical environments.

Planned Activities

The remainder of Year 1 will focus a systematic study of ICP-CRS optimization and the determination of detection limits. Parallel to this, design of the GF-CRS interface will begin. In Year 2, evaluation of the argon ICP-CRS will be completed. Preliminary experiments will begin on the viability of using air-ICP-CRS as a, for example, Hg CEM monitor. System optimization of the GF-CRS option will begin. These experiments will continue through Year 3 resulting in a complete evaluation of CRS as an analytical atomic spectroscopic tool.

Information Access

1. G. Miller and C.B. Winstead, "Inductively Coupled Plasma-Cavity Ringdown Spectroscopy," Journal of Analytical Atomic Spectrometry 12, 907 (1997).
2. C.B. Winstead, P.R. Jang, and G.P. Miller, "Continuous Emission Monitoring Using Cavity Ringdown Spectroscopy," 34th Symposium on Engineering Aspects of Magnetohydrodynamics, Starkville, Mississippi, June 18-20, 1997.
3. C.B. Winstead and G. Miller, "Detection Limits for Selected Metals by ICP-CRS" In Prep.
4. W.J. Price, Analytical Atomic Absorption Spectroscopy, Heyden & Son Inc., New York (1972).

High Fluence Neutron Source for Nondestructive Characterization of Nuclear Waste

Mark M. Pickrell, Los Alamos National Laboratory

Research Objective

We are addressing the need to measure nuclear wastes, residues, and spent fuel in order to process these for final disposition. For example, TRU wastes destined for the WIPP must satisfy extensive characterization criteria outlined in the Waste Acceptance Criteria. Similar requirements exist for spent fuel and residues. At present, no nondestructive assay instrumentation is capable of satisfying all of the requirements. One of the primary methods for waste assay is by active neutron interrogation.

We plan to improve the capability of all active neutron systems by providing a higher intensity neutron source (by about a factor of 1,000) for essentially the same cost, power, and space requirements as existing systems.

This high intensity neutron source will be an electrostatically confined (IEC) plasma device. The IEC is a symmetric sphere that was originally developed in the 1950s as a possible fusion reactor. It operates as D-T neutron generator. Although it was not believed to scale to fusion reactor levels, these experiments demonstrated a neutron yield of 2 x 1010 neutrons/second on table-top experiments that could be powered from ordinary laboratory circuits (1 kilowatt). The basis for scaling the output up to 1x1011 n/s has been established. In addition, IEC devices have run for cumulative times approaching 10,000 hours. The essential features of the IEC plasma neutron source, compared to existing sources of the same cost, size and power consumption, are: neutron yield of 1011 compared to 108, lifetime of 10,000 hours compared to 500, and operation is pulsed or steady state compared to pulsed.

The design of a conventional IEC source is a spherical vacuum chamber containing a spherical grid. The grid is raised to a high negative potential. A breakdown develops between the chamber wall and the grid, and this plasma becomes a source of positive deuterium and tritium ions. These ions are accelerated to the center of the vacuum chamber sphere where they may collide. If the grid is raised to a nominal 100 kV, the coulomb barrier for D-T fusion, then the fusion cross section becomes quite large and the neutron production proceeds. The limiting factor has been high densities associated with the Paschen breakdown curve. Because of the high densities, the ions tend to collide multiple times before reaching the center and do not collide with the full accelerating potential. The Los Alamos IEC uses a triple grid design. In the triple grid IEC device, the inner grid is the accelerating grid and serves the same function as the single grid in conventional IEC systems. The central grid serves as electrical isolation, and is held at ground potential. The outer grid is raised to a modest positive potential, say 200 volts. Dispenser cathodes around the vacuum chamber wall inject electrons. The electrons are trapped and orbit around the outer grid, ionizing a local plasma. Because of the modest potential, the breakdown occurs at a different point on the Paschen curve, at a much lower density. The limit is further relaxed by the injected ionization from the dispenser cathodes. The result is a lower density plasma. The result is a tight focus of fully accelerated ions that collide in a beam-beam mode. The collision energy and neutron yield are large.

Research Progress and Implications

As of May, 1998, we have completed the construction of the IEC experiment, tested the initial plasma breakdown, and modified the experimental chamber. These activities were all part of the original experimental plan and are reflected in the milestone table below. A picture of the IEC experiment is shown below. The main effort so far has been the construction of the experimental facility. That work required the entire first year and larger funding than in subsequent years. The IEC experiment was completed on budget and ahead of schedule. The vacuum chamber, power supplies, gas system, vacuum system, and control electronics were all completed and tested.

This year the focus has been on initial plasma studies and plasma breakdown. The key to the IEC experiment is the breakdown conditions. The object is to achieve breakdown at lower densities so that the plasma is less collisional and the accelerated ions travel all the way to the center before colliding. Therefore, we have experimented with the vacuum chamber design in order to achieve the low density breakdown. As a result of these studies, the high voltage grid design and the electron injector design were modified. These changes were made to optimize the neutron performance.

The Los Alamos IEC design is significant. IEC research has been conducted for over 3 decades, but always with a single grid. All previous attempts have suffered from high density, marginal neutron output, and limited lifetime because of neutral particle sputtering. All of these effects are due to the high plasma density. The Los Alamos design has already shown it can achieve lower densities. What remains is to operate the device at high voltage and maintain the low densities. During these operations we will also measure neutron yield in deuterium, which is a factor of 100 lower than for the D-T mix. We intend to optimize performance in deuterium to achieve 109 n/s, which is equivalent to the goal of 1011 n/s in D-T.

Planned Activities

We plan to continue the research program that was originally outlined in our proposal. The revised plasma chamber is complete. Our next step is to begin producing neutrons in a D-D environment

and optimize neutron production and system lifetime. Once we have fully optimized output from D-D (hopefully to the level of 109 neutrons / second), we will seal the vacuum chamber and attempt to run with tritium and achieve the goal of 1011 n/s. Once we have defined the physics and operating parameters, we will re-engineer the system with a commercial partner in order to make this a commercial product that can be used in a wide range of nondestructive assay (NDA) systems. Having a commercially-available system is crucial to the deployment of this technology as well as the incorporation of it into future NDA systems.

Ion and Molecule Sensors Using Molecular Recognition in Luminescent, Conductive Polymers

Michael R. Wasielewski, Argonne National Laboratory

Kenneth Raymond, University of California, Berkeley
David R. Walt, Tufts University

Research Objective

The purpose of this project is to develop sensor technology for detecting specific heavy metal ions, such as transition metals, lead, lanthanides, and actinides in waste streams. The sensing strategy uses molecular recognition of the metal ions by polymers that change their luminescence and conductivity properties upon metal binding. Research problems that are being addressed by this project include: 1) designing molecular recognition sites that are highly selective for the metal ions of interest in the presence of a large background of other chemical species, 2) finding ways to incorporate many different selective groups into a single polymer, 3) fabricating polymer films, strips, sheets, and coatings that can be applied to other materials, such as fiber optics and surfaces, 4) developing interfaces between the polymers and substrates that can be used to produce prototype arrays of many sensor elements for rapid multi-contaminant detection and quantitation, and 5) developing multiplexed data collection techniques to rapidly process the data obtained from many polymer sensors into a chemical profile of a waste stream or waste site in real time.

Research Progress and Implications

As of June 1, 1998, we have prepared several polymers based on the incorporation of 2,2'-bipyridine into poly(phenylenevinylene) polymers. The central idea, illustrated in Figure **1**, is to prepare a

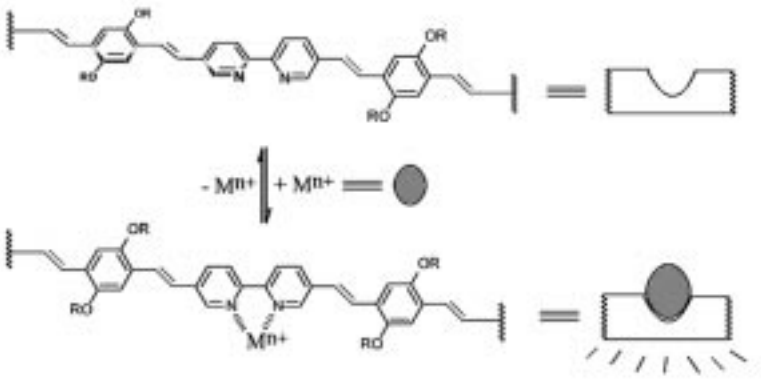

Figure 1**. Metal binding results in conformational changes in the conjugated polymers.**

pseudoconjugated, ligand-containing polymer that upon incorporating metal ions undergoes a conformational change, thus converting the initial partially conjugated polymer to a fully or near fully conjugated one. Such conjugation enhancement,along with the simultaneous electron density change caused by incorporating metal ions onto the backbone of polymers, dramatically changes the optical and conductivity properties of the polymer. These property changes are used to signal the presence of the metal ion analyte. We have developed several synthetic routes to these polymers and have demonstrated that they exhibit selective binding properties when exposed to transition metals and lanthanides. In addition, we have developed a new polymer that gives us the versatility that we need for rapid attachment of ligands that bind heavy metals, such as lead and plutonium. This polymer has reactive ester groups that can be used to append other ligands to a pre-formed conjugated polymer backbone.

We have prepared ligands that are specific for iron, plutonium (IV), uranyl, and lead ions, which are highly suitable for incorporation as molecular recognition sites in the polymers. This work has addressed two important questions regarding the incorporation of multidentate metal-ion specific sequestering agents into sensor materials. The first question was whether it was feasible to attach such ligands (specifically, Pu(IV) sequestering ligands) to the polymer, and the second question was to what extent these ligands need to be preorganized in order to exhibit discriminate binding of metal ions. Four different Pu(IV) sequestering ligands were attached to a Merrifield resin. Extraction experiments with these materials demonstrated their high efficiency at Pu(IV) complexation as well as high selectivity over simultaneously present Fe(III) which has similar complexation behavior. It appears that the presence of tetradentate ligand groups (containing two bidentate units each) is sufficient to provide strong and selective binding of Pu(IV).

We developed photoinitiated polymerization reactions that serve to fix the poly(phenylenevinylene) polymers at well separated spots on the tip of a single optical imaging fiber. Polymer blends of the conjugated sensor polymer with either siloxane or 2-hydoxy-ethylacrylate polymers are used for this purpose. Addition of crosslinkers to the acrylate polymer makes it possible to trap the conjugated polymer within the structure of the acrylate. Crosslinking prevents swelling of the acrylate polymer in the presence of organic solvents, and thus prevents loss of the entrapped conjugated sensor polymer. We have demonstrated that the metal binding properties of polymer blends containing the conjugated polymers and either siloxane or 2-hydroxyethylacrylate polymers attached to the ends of fiber optics are very similar to those observed for polymer solutions. These results represent the achievement of a critical milestone which demonstrates that conjugated polymers in polymer blends offer a convenient and functional way in which to prepare prototype fiber optic sensors for metal ions.

Planned Activities

The following work is planned for the next year: derivatization of conjugated polymers with the new ligands that are designed specifically for actinides; the synthesis of well-defined conjugated oligomers of phenylenevinylene substituted with ligands for heavy metals; the use of pre-formed oligomers as additives in acrylate polymers for producing fiber optic sensors; functionalization of the sequestering agents that were developed for uranyl ions with the goal of providing a ligand that will make the properties of the conjugated polymers sensitive to the presence of the uranyl ion; synthesis of new ligands that make use of the stereochemical coordination properties of lead ions to produce polymer-compatible ligands that are sensitive to lead; investigations of the photoimmobilization of the oligomers and polymers on fiber optics using photo excitation of a particular region of the fiber to initiate selective binding to the fiber; testing of a prototype sensor on heavy metal and actinide groundwater contamination.

Other Access to Information

FY1997 Year-End Progress Report (14 pages with figures and references) M.R. Wasielewski

This report is available on-line at **www.chem.nwu.edu/~wasielew/homepage.html**

Development of Advanced In-Situ Techniques for Chemistry Monitoring and Corrosion Mitigation in SCWO Environments

Digby D. Macdonald, Pennsylvania State University

Karen M. Garcia, Idaho National Engineering and Environmental Laboratory
George Engelhardt, Pennsylvania State University

Research Objective

This report evaluates the two years results of our research on the development of advanced electrochemical techniques for use in supercritical water oxidation (SCWO) environments.

Research Progress and Implications

The SCWO technology was found to be a promising approach to treat a variety of hazardous wastes. However, the corrosion processes in the SCWO reactors is still a problem for further development of this technology. We have developed a flow-through electrochemical cell (FTEC) which allows us to monitor the corrosion process in real time at temperatures up to 500°C and pressures up to 400 bar. The FTEC consists of a flow-through Ag|AgCl external pressure-balanced reference electrode, a flow-through platinum hydrogen electrode, an yttria-stabilized zirconia pH sensor and an electrochemical noise sensor. The new FTEC has been designed to serve as a measurement vessel for our high temperature and high pressure circulation once-through flow loop and titanium alloy was chosen as the construction material. The FTEC, shown schematically in Figure 1, is used for our experiments. Two HPLC pumps are employed in the system, one for pumping the reaction solution through the loop and the other for pumping the reference solution through the reference electrode. The system pressure is sustained as a constant via a back pressure regulator. The temperature was measured using a thermocouple installed at the center of the FTEC.

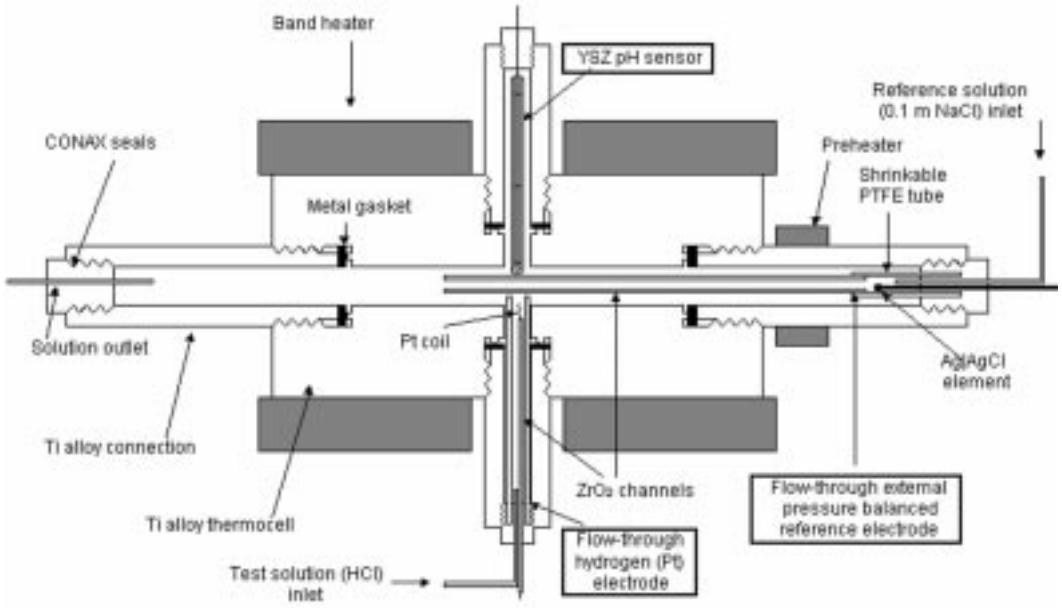

Figure 1. Diagram of the flow-through electrochemical cell (FTEC).

Because many physico-chemical processes, including corrosion, are sensitive to the pH, the measurement and control of pH is very important for the high temperature SCWO environment. We have measured [1] the potentials of the FTEC for several HCl(aq) + NaCl(aq) solutions of different concentrations of HCl(aq) and derived the corresponding pH differences (ΔpH) over a wide range of temperatures at pressure around 350 bar. Comparison of the experimentally derived and theoretically calculated ΔpH values presented in Figure 2 clearly demonstrates the ability to measure pH with a high accuracy (better than ±0.05 pH units). This result also shows the viability of the developed FTEC as a versatile potentiometric system for use at supercritical temperatures. During the next year of the project we will address the problem of electrochemical noise measurements and monitoring corrosion processes that occur on metallic materials exposed to super critical water.

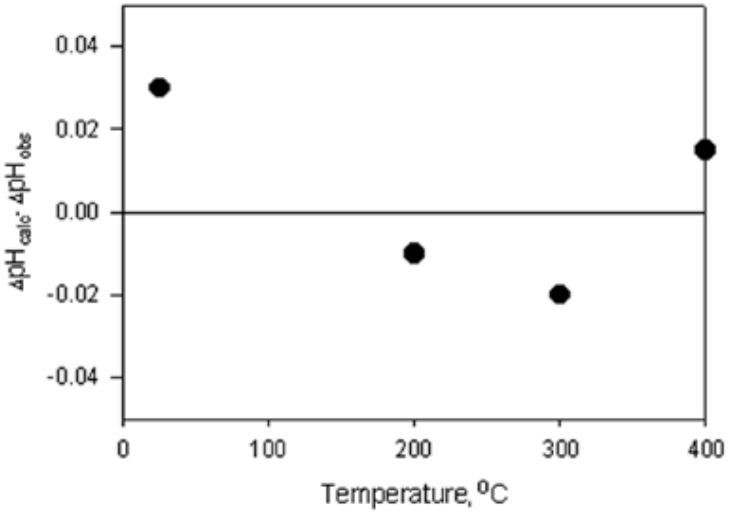

Figure 2. Comparison between theoretically calculated and experimentally measured differences in pH (ΔpH): ΔpH= pH(0.01mHCl+0.1mNaCl)-pH(0.001mHCl+0.1mNaCl).

[1] S.N. Lvov, X.Y. Zhou, and D.D. Macdonald, Potentimetrioc pH Measurements in Supercritical Aqueous Solutions, In: Proc. of the 193rd Meeting of the Electrochemical Society, San Diego, 1998, Abstr. No. 1016.

Planned Activities

During the next year of the project, we will address the problem of electrochemical noise measurements and monitoring corrosion processes that occur on metallic materials exposed to super critical water.

The Adsorption and Reaction of Halogenated Volatile Organic Compounds (VOC's) on Metal Oxides

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Research Objective

The goal of the research is to elucidate the properties of the materials responsible for the activation of halocarbons and the nature of the intermediates formed in the dissociative adsorption of this class of compounds. This information is essential for interpreting and predicting stoichiometric and catalytic pathways for the safe destruction of halocarbon pollutants. The specific objectives are: (1) to study the adsorption and reactivity of chloromethanes and chloroethanes on metal oxides; (2) to identify the reaction intermediates using spectroscopic methods; and (3) to develop kinetic models for the reaction of these halocarbons with oxide surfaces.

Research Progress and Implications

This report summarizes work after 20 months of a 36-month project. Emphasis has been placed understanding the surfaces phases, as well as the bulk phases that are present during the reactions of chlorinated hydrocarbons with strongly basic metal oxides. Most of the research has been carried out with carbon tetrachloride.

Surface Science Studies: The adsorption/reaction of CCl_4 with CaO. Ultra-thin CaO films were synthesized under ultrahigh vacuum (UHV) conditions by evaporating calcium onto a Mo(100) surface. The CaO films were grown at 400 K followed by annealing to 1000 K in an oxygen background to improve their crystalline quality. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) did not reveal the prsence of any impurities, including carbonate ions, on the surface. The ratio of the Ca to O XPS peaks was found to be nearly 1, indicating a nearly stoichiometric CaO film.

Temperature-programmed desorption (TPD) desorption spectra were acquired for Ccl_4 subsequent to increasing CCl_4 exposures on Ca/Mo(100) at 110 K. A single desorption feature was observed at 207 K. This feature shifted to 203 K and new desorption features developed at 167 K and 183 K as a function of the CCl_4 exposure. The desorption feature at 167 K shows characteristic zero-order behavior, indicating desorption from multilayer CCl_4. No desorption peaks associated with CO, CO_2, OCl, CaCl or $CaCl_2$ were observed. Furthermore, neither carbon nor chlorine was detected with AES and XPS after thermal desorption at 1000 K.

The Cl XPS spectra were obtained after CCl_4 adsorption at 110 K with increasing annealing temperature. XPS and AES measurements showed no carbon or chlorine signals after direct heating of the sample to 280 K, demonstrating that all CCl_4 and its fragments desorb from the CaO surface. The appearance of Cl peaks in the XPS spectra taken after annealing the sample to 800 K indicates that some irreversible photon-induced decomposition or reaction of CCl_4 occurred. Annealing the sample to 1000 K for 5 min apparently breaks the Ca-Cl bond followed by desorption of the chlorine ion or CaClx.

Destructive Adsorption of CCl_4 on Alkaline Earth Oxides: Destructive adsorption in this context involves the reaction of CCl_4 with a metal oxide to form the corresponding metal chloride and CO_2. The reaction has been followed over the alkaline earth oxides as a function of the amount of CCl_4 injected and the reaction temperature. By using XPS and Raman spectroscopy, it was found that the activity toward CCl_4 parallels the basicity of the oxide; i.e., the activity decreased in the order BaO>SrO>CaO>MgO. Barium oxide begins to react with CCl_4 at 200-300° C, and, at these low

temperatures, CO2 was the only gas phase product that evolved from the surface. At higher reaction temperatures, other oxides such as CaO and MgO also become active, and $COCl_2$ was found to be an intermediate. Although the destruction process is initiated at the surface, the continuous O_2^-/Cl^- exchange results in the bulk transformation of the metal oxide to the metal chloride. At higher temperatures, these solid state reactions involve an unusual alkaline earth metal oxide chloride; viz., M_4OC_{l6} (M=Ba, Sr or Ca).

With BaO it is possible to go through a reaction cycle by dissolving the chloride in water, followed by precipitation of the barium carbonate. Subsequent calcination of the carbonate results in the formation of the original oxide. Based on favorable thermodynamics, one can conceive of several catalytic cycles involving BaO. For example, the addition of H_2O to CCl_4 should result in the continuous formation of HCl and CO_2 as reaction products.

NMR Studies of the Reaction of CCl_4 with strongly Basic Oxides: Nuclear magnetic resonance (NMR) evidence suggests that sodium oxide and sodium peroxide may be superior to even barium oxide for the stoichiometric destruction of CCl_4 and $C_2H_3C_{l3}$. The reaction occurs at temperatures as low as 275° C. Cesium hydroxide also was surprisingly active, but solid sodium hydroxide was unreactive under similar conditions. The reaction of $^{13}CCl_4$ with BaO was followed in a rotor at temperatures between 25° C and 300° C. Heating the sample to 300 C caused the desorption of physisorbed CCl4 and the formation of CO_2, which is consistent with results obtained by FT-IR spectroscopy and gas chromatography. No other carbon-containing species were detected by NMR.

Planned Activities

Research will continue on the reactions of CCl_4 with thin films of well characterized oxides. On conventional oxides, emphasis will be placed on the catalytic destruction of CCl_4, either by reaction with H_2O or O_2. Elementary steps in the reaction cycle will be followed using in-situ FT-IR and Raman spectroscopies. NMR spectroscopy will be used to examine both the gas phase and the solid phase during stoichiometric reactions over alkali metal oxides, peroxides and superoxides.

Photooxidation of Organic Wastes Using Semiconductor Nanoclusters

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Research Objective

The photo-oxidation of toxic organic chemicals to carbon dioxide and dilute mineral acids using sunlight as an energy source and nanosize semiconductors to catalyze the process.

Research Progress and Implications

This report summarizes work after 1.5 years of a 3-year project. Our efforts have focussed on demonstration of photocatalysis of organic pollutants using nanosize MoS_2. We investigated the effects of :1)bandgap, valence and conduction band energies; 2)surface modification of MoS2 by deposition of metal and metal oxide islands to enhance electron transfer; and 3)use of semi-conductor semi-conductor composites to achieve improved charge separation and thus photooxidation of pollutants.

We synthesized and studied nanosize MoS_2 of three different sizes and associated bandgaps and studied photoredox reactions of nanosize MoS_2 dispersed in solution and supported on a macroscopic

powder. The latter would be the method of choice for use as a practical photocatalyst for water purification.

As we emphasized in our original proposal, MoS_2 in nanosize form can be tuned to absorb various amounts of the solar spectrum. We discovered there is an optimal choice of absorbance characteristics and valence and conduction band levels which allow the rapid photo-oxidation of a chosen organic molecule. The advantages of having a photostable material with a tunable bandgap were demonstrated in an experiment where phenol destruction with visible (>450 nm) light occurred at a dramatically faster rate with nanoscale MoS_2 catalysts compared to the best available previous material TiO_2. This was the first demonstration of rapid photooxidation of an organic molecule using a completely photostable catalyst and only visible light.

The possibility of transferring electrons or holes between nanoscale MoS_2 and other semiconductor materials in order to increase electron/hole lifetimes were explored. It was shown that small amounts (<5 weight %) of nanoscale MoS_2 deposited on to TiO_2 can lead to significant (~2) enhancements of phenol destruction rates.

Room Temperature Photo-redox Reactions: A number of different chemicals were photocatalyzed sucessfully to CO_2, but most of our work centered on the destruction of phenol. This particular organic was chosen for its ease of detection and relative resistance to oxidation, and because its photo-oxidation has been studied extensively by many previous researchers. No attempts were made to find the absolute quantum yield of the photo-oxidation process. Rather, following the approach of Serpone and coworkers we compared the relative activity of nanoscale MoS_2 to a well studied photocatalyst, Degussa P25 TiO_2.

Chemical analysis was done with high pressure liquid chromatography (HPLC) using a reverse phase column, Hewlett-Packard 1050 diode array detector, and Hewlett-Packard 1046A fluorescence detector. The fluorescence detector allowed detection of phenol to ~10 ppb without preconcentration. We were typically able to destroy phenol and certain cholorinated hydrocarbons such as pentachlorophenol (a common wood preservative) to undetectable levels in less than 2-3 hours of treatment.

A. Phenol Destruction With Visible Light

One of our primary reasons for examining MoS_2 nanoclusters was to try and find a nanoscale photocatalyst that is active when illuminated by visible radiation. We were quite successful in this regard. MoS_2 nanoclusters could photocatalyze the destruction of a difficult-to-oxidize compound with visible light. The fact that both the 8-10 nm MoS_2 with a 700 nm bandgap and 4.5 nm MoS_2 with a 540 nm bandgap samples are catalytically active suggests that their valence bands are sufficiently low to produce hydroxyl radicals that then oxidize phenol. 3.0 nm MoS_2 with a bandgap of 420 nm was also effective but required light in the range 360-420 nm to work efficiently.

B. MoS_2 Supported Catalysts

Catalytic materials are often times deposited on to support materials. This is done not only to prevent the catalyst from agglomerating, but often times because reaction rates can be synergistically increased through interactions between the catalyst and support material. Semiconductor photocatalysts are no exception to this behavior, and for MoS_2 nanoclusters, deposition on a support material may prevent adverse chemical changes as well. Another twist in this vein for semiconductor photocatalysts is the possibility of electron or hole transfer between two semiconductor catalysts, which we have recently shown (see below) leads to enhanced electron-hole lifetimes, and faster reaction rates.

A series of experiments where 8 nm MoS_2 nanoclusters with a bandgap of ~700 nm were deposited on to powders TiO_2, SnO_2, WO_3, and ZnO were performed. The deposition method was remarkably simple. Powdered support material was mixed into a solution of MoS_2 nanoclusters and then centrifuged with a vacuum applied. The solution slowly evaporated leaving nanoclusters deposited on to the support material. No heating or other treatments were performed, so further enhancement of contact interactions between the nanoclusters and semiconductor support material is possible (see future directions). In all cases, between 0 and 6 weight percent MoS_2 nanoclusters were deposited on to the support. The reaction rate for destruction of 20 mg/l phenol was then measured with a total (MoS_2^+ support) catalyst density of 2 gm/l.

We found that MoS_2 nanoclusters had a significant enhancement of catalytic activity under the conditions described above, when deposited onto TiO_2. The other metal oxide powders were much less effective, and most showed some photodegration themselves-which may rule them out as practical support materials. . The destruction rate was enhanced up to a factor of ~2 when the loading was ~2.5 weight percent. When the 8 nm sized MoS_2 was not loaded on to TiO_2, however, the phenol destruction rate was much smaller than the enhancement achieved when it is loaded. These observations strongly suggest that electron or hole transfer is occurring between the TiO_2 and nanosize MoS_2. We hypothesized in our original proposal that we could take advantage of this synergism to enhance pollutant destruction rates significantly, and we have now established this fact.

The decrease in the reaction rate for loadings greater than 2.5 weight percent of nanosize MoS_2 is somewhat puzzling. There are apparently two competing processes occurring when 8 nm MoS_2 is loaded on to TiO_2, one which enhances phenol destruction and another which impedes it. A possible scenario which would explain this data is that a small amount of nanosize MoS_2 enhances phenol destruction through electron or hole transfer processes, but that excess amounts of MoS_2 impede phenol destruction by blocking important phenol binding sites on the TiO_2 surface. This has given us new ideas for support materials for nanosize MoS_2 (see future directions).

Time-Resolved Electron and Hole Transfer Studies

During this period we have focused on the study of interfacial electron transfer in hybrid semiconductor nanoclusters. Specifically, the MoS_2/TiO_2 and WS_2/TiO_2 hybrid nanoclusters have been synthesized and studied. The dynamics were studied using time-resolved laser spectroscopy.

The MoS_2/TiO_2 or WS_2/TiO_2 hybrid nanocluster emission kinetics were compared to those of the appropriate control, lacking TiO_2. In all cases, the kinetics consist of a very fast component and a slower, nonexponential component. The fast and slow components are assigned to electron/hole recombination from deep and shallow traps, respectively.

In the WS_2 case, the presence of the TiO_2 reduces the t=0 emission intensity, and results in a somewhat faster decay of the slow component. The decrease in the t=0 emission, along with a decrease in the total emission intensity, may be interpreted in terms of electron transfer from the WS_2 conduction band, prior to electron trapping. These processes are very fast. In other systems, trapping has been shown to occur on the sub-picosecond timescale. These results suggest that electron transfer from the conduction band occurs on a similar timescale. The increase in the decay rate of the slow component may be interpreted in terms of electron transfer from the shallow traps. This electron transfer occurs on a much slower 10's of ps timescale, the same timescale as trapped electron/hole recombination. Little or no change is observed in the fast component, suggesting that electron transfer does not occur from the deep traps. These effects are fairly small, but quite reproducible, with the quantum yield for electron transfer being only about 20%. The implication is that we can dramatically improve electron transfer rates with these hybrid systems.

Planned Activities

The key to viable use of sunlight to destroy organic pollutants in water systems is significant and continuous improvements in our nanosize MoS_2 photocatalysts via pre-treatment and or chemical modification. We intend to study the effect of heating our MoS_2/ TiO_2 semiconductor hybrid nanoclusters to increase physical contact between the semiconductors and thus increase electron/ hole transfer rates. New chemical modifications to the surface of the nanosize MoS_2 will also be explored. By analogy with highly active MoS_2-Co/Ni hydrotreating catalysts, we intend to deposit islands of base metals such as Co, Ni and Fe on nanosize MoS_2 and investigate the photocatalytic behavior.

Another key idea we will explore is the use of nanosize MoS_2 supported on high surface area carbon. The concept is to exploit the high surface area and known favorable adsorbtion characteristics of carbon towards organics with the demonstrated visible photocatalytic oxidation of these organics by nanosize MoS_2. This might allow continuous regeneration of a "clean" carbon surface-eliminating the current necessity to dispose of contaminated carbon as occurs when all surface sites become occupied by pollutants.

It has also been convincingly shown recently (Tributsch, Science March 1998) that certain other metal sulfides are particularly resistent to oxidative degradation in bulk form-namely RuS2 and PtS2. Unfortunately, the bandgaps of these materials, like MoS_2, are too narrow to efficiently photooxidize organics. We expect that a synthesis of these materials in nanosize form will shift their bandgaps into the visible and make them possible photocatalyst candidates. We intend to synthesize them for the first time in nanosize form and test them singly and as hydrid combinations with nanosize MoS_2.

D.F. Kelley will be continuing his studies of electron and hole transfer using time-resolved PL and absorbance to better understand the chemical and structural features which influence high photocatalytic activity in nanosize MoS_2 and WS_2.

Nuclear Materials

Aqueous Electrochemical Mechanisms in Actinide Residue Processing

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Research Objective

New and/or improved solutions to the stabilization and volume reduction of nuclear materials processing residues are urgently needed. Mediated electrochemical oxidation / reduction (MEO/R) processes are one such approach for incinerator ash, combustibles, and other solid residues. However, questions remain concerning the mechanisms of these processes, and how they might be optimized. In addition, further research is merited to extend their range of applicability. Recent advances in the study of heterogeneous electron transfer in solid substrates have opened the door for the re-examination of electron transfer processes associated with redox mediated actinide dissolution. We will develop a deeper understanding of the thermodynamic and mechanistic aspects of heterogeneous electron transfer that lie at the heart of these MEO/R processes. We will also develop and test new approaches based on the results of these fundamental studies using actual residue materials. Key aspects of this proposal include:

- Determination of the potential windows for oxidation / reduction of colloidal actinide oxides and actinide-bearing oxide and organic substrates and the e—transfer kinetic parameters that govern the current - overpotential characteristics.
- Development of adaptations of mediation schemes and application of co-mediation reagents for oxidative and reductive dissolution based on complexation of the surface-bound or solid-phase actinides and/or the dissolved redox mediator.
- Execution of bench-scale tests of new MEO/R schemes on actual residue materials

Research Progress and Implications

This report summarizes work after 8 months of a 3-year project. Progress to date falls into three categories as discussed below:

Materials and equipment procurement: A new computer-controlled potentiostat was procured and tested for work with solid and Hg electrodes. A consensus was established among investigators regarding the metal-oxide substrates to be used in the initial phase of this project for actinide sorption and electrochemical characterization. TiO_2 and SiO_2 were selected and these materials were procured. Manufacturer characterization data have been compiled and in-house characterization (e.g., powder XRD) has been undertaken. Computer codes for digital simulations of electrochemical response functions have also been upgraded and ported into desk-top applications.

Detailed literature investigations: Background information was compiled on key experimental parameters for sorption and desorption studies, including selection of substrate and examination of surface physical characteristics. Although TiO_2 may be prepared by a variety of methods, its surface composition, structure and pHpzc (5.6-6.5) do not vary significantly. Some literature reports of uranium (UO_2^{2+}) uptake on titania have appeared, which suggest that sorption increases as a function of pH below pH 5-6, and then drops off at higher pH values. While little is known about the possible modification of surfaces with organic species (e.g., complexants), it is known that inorganic ions (e.g., PO_4^{3-}, SO_4^{2-}) may be absorbed under certain conditions, and TiO_2 will sorb CO_2 through a range of pH conditions. These anion affects have been demonstrated to alter metal uptake profiles.

Another variable is the redox potential of possible mediators. There are reports that the potential of the Ce(IV/III) couple may be altered significantly by counterion. For instance, the oxidation potential of Ce(III) can vary from +1.7 V (vs. NHE) in 1M $HClO_4$ to +1.4 V in 1M H_2SO_4. Upon coordination by stronger donor ligands a significant cathodic shift in redox potential may be observed. This effect has been employed to stabilize Ce(IV) in certain coordination environments, and the oxidation potential can be shifted by as much as 1 V. For organic complexants, redox potentials can also be "tuned" by variation of substituents. For instance, in a series of N,N'-ethylenebis(salicylidene-amine) ligands shifts in the Ce(IV/III) couple of 250 mV can be induced by variation of a single substituent. There is less evidence that simple complexants can be used to control the redox potential of other ions commonly used in mediated electrochemical reactions (e.g. Ag^{2+}, Co^{3+}). It is possible, however, to synthesize organometallic or inorganic coordination complexes of these ions with favorable redox characteristics. For instance, a series of substituted Ag(II) porphyrin complexes may be readily oxidized on either the spectroelectrochemical or chemical time scale without demetallation. Similarly, the cobaltocene ($Co(C_5H_5)2$)/cobaltocenium redox couple is commonly employed in redox reactions in non-aqueous media; adaptation of this reagent to aqueous solution is possible through sulfonation of the carbocyclic ligand.

Preliminary results: One aspect of this work is the determination of formation constants between complexing agents and both dissolved actinide elements and electron transfer mediators. A standard way to obtain this information involves the precise measurement of shifts in electrochemical potential with addition of the complexant. Accuracy is critically dependent on a stable reference electrode. The highly acidic media necessary for some parts of this project precludes the use of standard reference electrodes, such as Ag/AgCl and saturated calomel, due to the constantly changing liquid junction potential and the precipitation of salts at the reference electrode-test solution interface. To overcome this problem we tested several reference electrode combinations, finally settling on a modified silver-silver chloride double junction electrode for use in strongly acidic, perchloric acid based media. The electrode consists of a Ag metal in contact with an internal filling solution of 5.0 M sodium perchlorate and 0.1 M silver perchlorate. A porous membrane connects this solution to an outer filling solution containing 5.0 M sodium perchlorate. Studies on the complexation of iron(II) and iron(III) with chloride in varying concentrations of perchloric acid demonstrated the required stability and accuracy of this reference electrode system.

Preliminary studies have been undertaken to determine the range of redox potentials and heterogeneous electron-transfer kinetic parameters for U(VI/V) and other uranium redox transformations as a function of solution conditions (1 M acid to 3 M base) and coordination environments (CO_3^{2-}, EDTA, etc.). Over this acid/base range the U(VI/V) redox couple shifts from ~ -0.1 V vs Ag/AgCl to ~ -1.0 V. The e—transfer rate constant (k0) likewise changes from fast (immeasurable by voltammetry) in acid to slow (~ 0.005 cm/s) in concentrated base. Coordination of UO_2^{2+} by ligands other than H_2O or OH^- moves the U(VI/V) couple to values intermediate between acid and base regimes and there is substantial variability in the e—transfer kinetics.

X-ray absorption spectroscopy (XAS) spectra of plutonium (Pu) in PuO_2, in a boroaluminosilicate waste glass simulant, and in calcined Rocky Flats ash were collected at the Stanford Synchrotron Radiation Laboratory. Plutonium in the glass and the ash is present as Pu(IV), and exhibits the PuO_2 structure. The Pu(IV) oxide in the glass exhibits significantly reduced order relative to the PuO_2 reference material. In contrast, the oxide in the ash is extremely well ordered, indicating that calcination of Pu loaded ash effectively converts all Pu to PuO_2, without formation of solid solutions with other oxides.

Planned Activities

Fiscal Year 1998(remaining): (a) Complete sorption experiments of actinides with SiO_2 and TiO_2. Characterize these solid phases by spectroscopy and microscopy. (b) Conduct heterogeneous electron transfer studies with these colloidal materials using potentiostatically-controlled metallic electrodes. (c) Begin heterogeneous electron transfer studies with colloidal materials and dissolved-phase redox mediators.

Fiscal Year 1999: (a) Complete heterogeneous electron transfer studies with these colloidal materials using potentiostatically-controlled metallic electrodes. (b) Continue heterogeneous electron transfer studies with colloidal materials and dissolved-phase redox mediators. (c) Conduct studies of the effects of actinide complexing agents (surface and dissolved) on dissolution using metallic electrodes and dissolved redox mediators. (d) Conduct solution speciation and surface complexation studies of reactant systems with and without actinide complexants. (e) Initiate scale-up studies of new mediator systems using incinerator ash as the residue stream.

Thermodynamics of the Volatilization of Actinide Metals in the High-Temperature Treatment of Radioactive Wastes

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Research Objective

In this project, we will perform a detailed study of the volatilization behavior of U, Pu and possibly Am and Np under conditions relevant to the thermal treatment (destruction) of actinide-containing organic-based mixed and radioactive wastes. The primary scientific goal of the proposed work is to develop a basic thermochemical understanding of actinide volatilization and partitioning/speciation behavior in the thermal processes that are central to DOE/EM's mixed waste treatment program. This subject addresses several technical needs/problem areas recently identified by DOE/EM's Office of Science and Technology. In the Low-Level and Mixed Low-Level Waste problem area, emission-free destruction of organic wastes is listed as the first exemplary science need. In the TRU Waste, Plutonium Materials, and Spent Nuclear Fuel problem areas, interactions between actinides and organic residues and materials stabilization are listed as exemplary science needs. Both of these needs require high-temperature thermodynamic studies of actinides and actinide-organic interactions.

A sound basis for designing safe and effective thermal treatment systems and the ability to allay public concerns about radioactive fugitive emissions are the principal benefits of the project. The proposed work is a combination of experimental studies and thermodynamic modeling. Vapor pressure measurements will be made to determine U, Pu and possibly Am volatile species and the extent of their volatilization when UO_2/U_3O_8, PuO_2 and AmO_2 solids are heated to temperatures of 500 to 1500°C under pyrolyzing (reducing) conditions or under oxidizing conditions (i.e. $O_2(g)$ + $H_2O(g)$ mixtures) in the presence of chlorine ($Cl_2(g)$ or HCl(g)). Work on uranium volatilization under reducing conditions will be performed in a laboratory at U. C. Berkeley in a collaboration with Professor D. R. Olander. In parallel with the experimental effort, a complete thermodynamic database for expected actinide gaseous species will be developed from literature data, from the proposed measurements, and from data predictions using bond energy correlation and statistical thermodynamics estimation methods.

Research Progress and Implications

This report summarizes work performed since October 1, 1997 in the first year of a 3-year project.

In December 1997, we put in place a small sub-contract at UC Berkeley to allow Professor D.R.Olander and a graduate student to begin work on uranium volatilization under reducing/gasification conditions. During this time a transport apparatus has been designed and built, and it is

currently being activated. A method for the determination of small quantities of uranium on collection foils using neutron activation has been selected, and several methods for preparing organic chars containing uranium oxide have been evaluated. The most promising char preparation approaches involve as first steps (i) incorporating dry uranium compounds into epoxy cements and (ii) loading uranyl ions onto suitable ion exchange resins. We are also trying to obtain small quantities of a uranium porphyrin compound such as bis(phthalocyaninato) uranium(IV) to serve as a model transportable specie.

Preparations for the planned plutonium volatility measurements have been somewhat slower than originally planned due to the need to change the facility in which the measurements will be conducted (the main Pu facility at LLNL has been shut down for several months) and the slow process of hiring the scientist identified for this project. To date we have identified and secured a location for this work in a suitable facility (B-151), we have prepared the necessary work plans and are well along in the approval process, and we have ordered the necessary equipment for the Pu transpiration experiments (glovebox, furnace, controllers, gas flowmeters, etc). A job offer has been made to a PhD chemist who has experience with transactinide element thermochromatographic behavior.

We initiated our effort to compile a complete thermodynamic database for potential actinide vapor species by estimating key thermodynamic parameters for species such as $AnO_3(g)$, $AnO_2(OH)_2(g)$, $AnO_2Cl_2(g)$ and $AnO_2F_2(g)$, where An=Np and Am, and $UO_2Cl(OH)(g)$, $UO_2F(OH)(g)$ and $UO_2FCl(g)$. These estimations extend previous thermodynamic predictions we have made for uranium and plutonium vapor species. Two papers that describe this and related work are being prepared for publication in the Journal of Nuclear Materials.

Planned Activities

During the remainder of the current fiscal year (June - September 1998), we will initiate and conduct several of the experiments designed to characterize uranium volatility under reducing conditions. The principal objective of these tests will be to determine whether there is any evidence for enhanced uranium volatilization due to the formation of organouranium compounds in chars at elevated temperatures. If such evidence is obtained, these experiments will be continued through FY99 with the aim of identifying the responsible specie(s). Equipment for the planned plutonium volatility experiments will also be assembled and commissioned during the remainder of FY98, and we are aiming to begin activation of the equipment (with uranium compounds) in September 1998. Transpiration experiments with Pu, Am, and possibly Np, compounds will be conducted through FY99 and FY2000. Throughout the remaining period of this project we will continue to estimate key thermodynamic parameters for actinide vapor species of interest and to develop the database that will be used in thermochemical prediction models.

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

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Research Objective

The objective of this research is to gain a fundamental understanding of the distributions and the solubility limits for actinides Pu and U and rare earth neutron absorbers such as Gd and Hf in waste forms. This will be accomplished by systematically studying the local structural environments of these constituents in representative waste forms such as glass, ceramics, and vitreous ceramics. Basic knowledge of these issues will provide a technical and scientific basis that can be used by the U.S. Department of Energy (DOE), Environment Management (EM) Program in developing, evaluating, and selecting waste forms for the safe disposal of Pu, spent nuclear fuel, and other transuranic wastes. The work presented here is a summary of our research activity from November 1997 to May 1998. The elucidation of the correlations between the local structural environments of actinides and rare earth neutron absorbers in waste forms as functions of waste form compositions, and waste form processing conditions will also advance basic material science.

Research Progress and Implications

The work presented here is a summary of our research activity from November 1997 to May 1998. Currently being studied is the effect of the Pu oxidation state on its solubility in borosilicate-based glasses. When glasses are melted in ambient atmosphere, Pu(IV) has been shown to be the dominant oxidation state as determined by ultraviolet-visible-near infrared spectroscopy (UV-VIS-NIR) and x-ray absorption fine structure (XAFS) techniques. However, no literature data are available for glasses containing Pu predominantly as Pu(III) nor the solubility for Pu(III) in the glass. The results of our study demonstrate that in borosilicate glass, Pu(III) is significantly more soluble than Pu(IV). Using x-ray diffraction analysis the solubility of Pu(III) as oxide was determined to be at least

25 mass% in the reduced glass, while it was no greater than 10 mass% in the same glass under oxidizing conditions (glass melting temperature was 1400°C). The oxidation states of Pu in the glasses were determined by XAFS analysis using the Pu L_{III} edge as shown in Figure 1. Using standard reference XAFS spectra of Pu(IV) and Pu(III), we estimated that about 90 % of the Pu was present as Pu(IV) in the oxidized glass and about 95% of the Pu was Pu(III) in the reduced glass.

In contrast to the redox effect on the solubility limit of Pu, the solubility of U in soda-lime (SL) silicate glass is favored under oxidizing conditions or glass with high Na_2O concentration. In ambient atmosphere at 1500°C, the solubility, in terms of UO_3, is found to be 30 mass% in the baseline glass (SRM 1830 from NIST) and at least 40 mass% in the baseline glass with additional Na_2O.

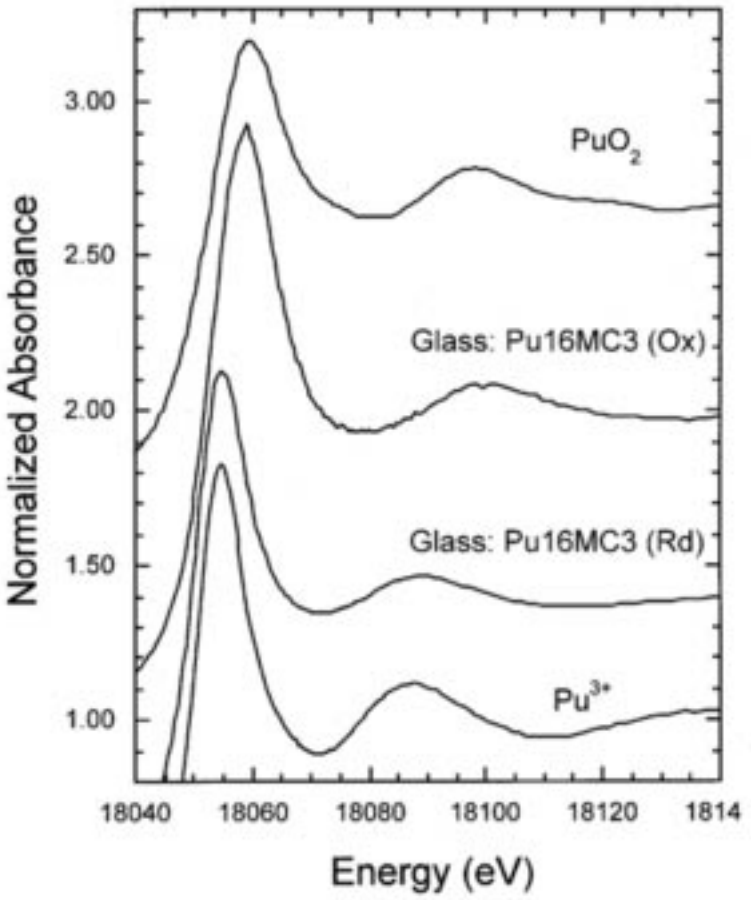

Figure 1. **Normalized Pu L_{III} near edge spectrum from a borosilicate glass with 10 mass% Pu oxide (Ox and Rd represent oxidized and reduced glasses, respectively)**

The local structural environments of U in the silicate glasses have also being studied with XAFS. Figure 2 shows U L_{III} x-ray absorption spectra of the SL glasses with various concentrations of U and melted under two different conditions. Glasses doped with 10 to 40 mass% UO_3, excluding glasses prepared under reducing conditions, yielded remarkably similar spectra, except for the systematic increase in white line intensity with U content. The oxidation state of U in the oxidized SL glasses more closely resembles that of U_3O_8 than UO_2. In contrast, the overall line shape, energy position, and presence of the actinyl signature indicate that U in the SL-U40AR glass is nearly all tetravalent and in the SL-U40R glass that a significant fraction is tetravalent. Furthermore, the extended XAFS clearly identifies the U(IV) in the reduced glasses from U-U scattering as UO_2. The estimated average valence of U in the oxidized glasses is five compared with a value about four in the reduced glasses.

The solubility and distributions of Gd and Cs in yttria-stabilized zirconia single crystal and polycrystalline zirconolite are being studied with ion beam implantation. Direct observation of the

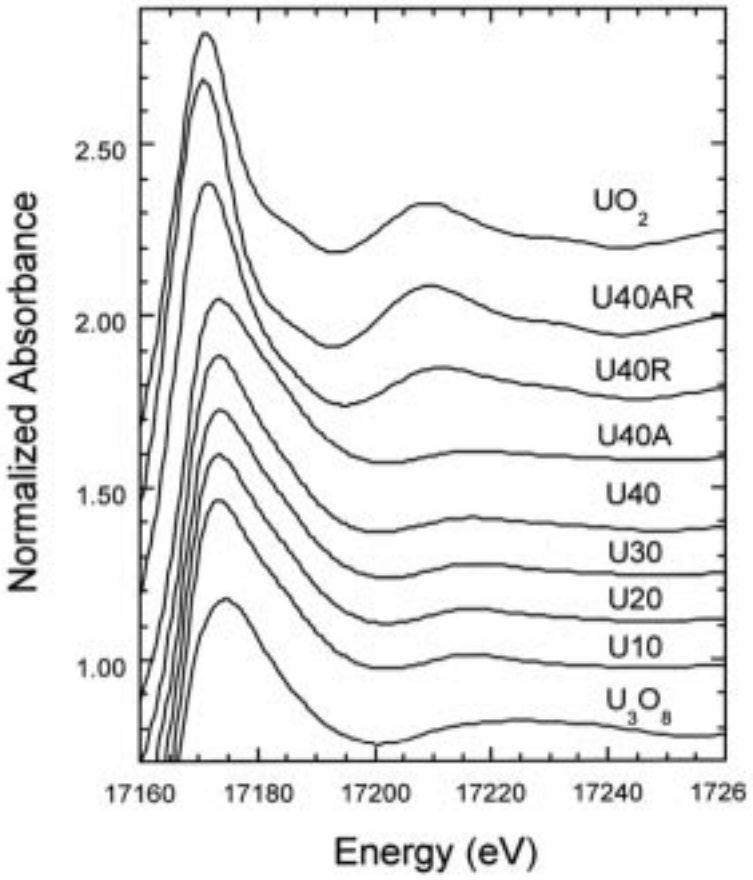

Figure 2. **Normalized U L_{III} near edge spectra from soda-lime glasses with various concentrations of U (U10-40: U concentrations in the SL glasses, R: reduced SL glasses, A: the SL glass with high Na_2O content)**

dynamic microstructure change during ion implantation was made using in-situ transmission electron microscopy. Amorphization of zirconolite was observed at room temperature after a dose of < $3x10^{14}$ ions/cm^2 of Cs^+. After $5x10^{16}$ ions/cm^2, ~5 nm precipitates were observed. With the implantation of an additional $5x10^{16}$ ions/cm^2 of Cs^+ at 500°C above the critical amorphization temperature of zirconolite; the amorphous zirconolite crystallized from the undamaged deeper region. The precipitates grew slowly in size to ~20-30 nm and their density increased to ~10^{15}/cm^3.

Planned Activities

The XAFS study for Pu and U in silicate and borosilicate glasses is on-going. The results obtained from the above studies will assist in the elucidation of the structural roles of Pu and U in the glass, which are critical for a better understanding of their solubility limits in the glasses. Studies of glass compositional and structural effects on the solubility limits of U, Pu, and rear earth neutron absorbers and U/Pu redox chemistry in crystalline waste forms have been initiated. These studies are projected to be completed within about two and one-half years.

Chemical and Ceramic Methods Toward Safe Storage of Actinides Using Monazite

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Lynn A. Boatner, Oak Ridge National Laboratory

Research Objective

To study the ceramics of monazite (specifically lanthanum monazite), enabling its use as a sequestering host for actinides (plutonium) and other radioactive nuclides. To demonstrate that monazite is a practical and reasonable solution to this problem.

Research Progress and Implications

This report summarizes work after 1-1/2 year of a 3-year project.

Introduction

The use of ceramic monazite, (La,Ce)PO_4, for sequestering actinides, especially plutonium, and some other radioactive waste elements (rare earths e.g.) and thus isolating them from the environment has been championed by Lynn Boatner of ORNL. It may be used alone or, as it is compatible with many other minerals in nature, can be used in composite combinations. Natural monazite, which almost invariably contains Th and U, is often formed in hydrothermal pegmatites and is extremely water resistant - examples are known where the mineral has been washed out of rocks (becoming a placer mineral as on the beach sands of India, Australia, Brazil etc.) then reincorporated into new rocks with new crystal overgrowths and then washed out again - being 2.5-3 billion years old. During this demanding water treatment it has retained Th and U. Where very low levels of water attack have been seen (in more siliceous waters), the Th is tied up as new $ThSiO_4$ and remains immobile.

Lest it be thought that rare-earths are “rare” or expensive, this is not so. In fact, the less common lanthanides such as gadolinium, samarium, europium, and terbium, are necessarily extracted and much used by, e.g., the electronics industry, leaving La and Ce as not-sufficiently-used by-products. The recent development of large scale use of Nd in Nd-B-Fe magnets has further exaggerated this. Large deposits of the parent mineral bastnaesite are present in the USA and in China. (Mineral monazite itself is not preferred due to its thorium content.)

In the last 5 years it has become apparent show that monazite (more specifically La-monazite) is an unrecognized/becoming-interesting ceramic material. PuPO4 itself has the monazite structure; the PO_4^{3-} unit strongly stabilizes actinides and rare earths in their trivalent state. Monazite melts without decomposition (in a closed system) at 2074° C and, being compatible with common ceramic oxides such as alumina, mullite, zirconia and YAG, is useful in oxidatively stable ceramic composites: for example, use is contemplated as an enabling weak interface in oxide-oxide fiber composites (including as a “high temperature starch” on space shuttle blankets), and possibly as machinable ceramics, friction materials and other. The ceramic behavior of pure and doped monazite has not yet been studied in any detail.

The sine-qua-non of ceramic studies and production is the reliable synthesis of reproducible starting powders and precursor chemicals that consistently reproduce the desired ceramic outcome. This has always been a more neglected (underfunded) side of ceramic studies; witness how many years passed before pure reproducible powders of alumina or silicon nitride became available for ceramic studies long after it was apparent that these were useful ceramics which, however, suffered from forming variation and degradation caused by small amounts of impurities.

Experimental and Results

We have 1) concentrated on the reproducible and automatic production of large quantities of La-monazite (up to the 10kg/week level). Several techniques have been tried to produce a heavy, weakly agglomerated, powder by aqueous precipitation of both monoclinic monazite and its hexagonal hydrated precursor rhabdophane, $LaPO_4.1/2H_2O$. The powders are such as to allow an automatic washing procedure in a newly designed "conical" washer. Fines are recycled as "seeds" to the precipitation step. It has been found that it is difficult to wash out some 2% excess phosphorus from the powders; a wash with tetramethyl ammonium hydroxide base remediates this. 2) We have studied the preparation of $LaPO_4$ from various water stable precursors such as:

(1) from La nitrate and phosphorous acid (N.B. phosphorous not phosphoric);
(2) from La nitrate and methyl phosphonic acid; and
(3) from La nitrate and phytic acid.

Of these (3) is likely the most important for nuclear waste or plutonium use due to its complexing ability.

Phytic acid, aka inositol hexaphosphate, is a poly-dibasic acid that forms acid soluble complexes with many cations which can be precipitated by raising the pH. It is readily available from seeds (soybeans, rapeseed, etc. - up to 100,000 tons a year could be produced as a by-product according to the Department of Agriculture) where it complexes important Mg, Ca and phosphate ready for germination. Thus, mixed with radioactive elements and La, it sequesters them; on heating, doped monazite is produced as a reactive powder for ceramic processing.

Studies of sintering/densification so far have shown that with 2% excess phosphorus the powders sinter readily via a liquid eutectic below 1200° C; coincident grain growth is rapid. The stoichiometric powder (i.e. exactly 1:1 La:P) sinters with difficulty but addition of, e.g., alumina encourages sintering. In other programs it has been discovered that monazite, surprisingly, shows low temperature plasticity. Not surprising then is that monazite can be fairly easily hot-pressed to high density at approximately 1200° C. Studies on hot pressed material are underway.

Planned Activities

We plan to continue the study of the ceramics (i.e., chemistry of powder, sintering, grain-growth, densification, etc.) of monazite, producing publications, so that the community has access to this knowledge.

Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms

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Alexandria Navrotsky, University of California at Davis

Research Objective

The end of the Cold War raised the need for the technical community to be concerned with the disposition of excess nuclear weapon material. The plutonium will either be converted into mixed-oxide fuel for use in nuclear reactors or immobilized in glass or ceramic waste forms and placed in a repository. The stability and behavior of plutonium in the ceramic materials as well as the phase

behavior and stability of the ceramic material in the environment is not well established. In order to provide technically sound solutions to these issues, thermodynamic data are essential in developing an understanding of the chemistry and phase equilibria of the actinide-bearing mineral waste form materials proposed as immobilization matrices. Mineral materials of interest include zircon, zirconolite, and pyrochlore. High temperature solution calorimetry is one of the most powerful techniques, sometimes the only technique, for providing the fundamental thermodynamic data needed to establish optimum material fabrication parameters, and more importantly, understand and predict the behavior of the mineral materials in the environment. The purpose of this project is to experimentally determine the enthalpy of formation of actinide orthosilicates, the enthalpy of formation of actinide substituted zircon, zirconolite and pyrochlore, and develop an understanding of the bonding characteristics and stability of these materials.

Research Progress and Implications

This report summarizes work after eight months of a three year project. Research efforts at UC Davis have focused on establishing the thermodynamic properties of zirconolite and pyrochlore, and the synthesis of other minerals relevant to storage of nuclear material. Heat capacity, entropy, enthalpy of formation, and free energy of formation data were established for zirconolite, $CaZrTi_2O_7$, in the range from 0 to 1500 K. The heat capacity, entropy, enthalpy of formation, and free energy of formation at 298 K for zirconolite are 211.9 J/K mol, 193.3 J/K mol, -3713.8 kJ/mol, and -3514.6 kJ/mol, respectively. Solution calorimetry experiments with cerium pyrochlore, $Ca_{0.8}Ce_{1.2}Ti_2O_7$, are complete. Heat capacity data and confirmation of the pyrochlore composition are required for final data analysis. Synthesis and characterization of $CaHfTi_2O_7$, $CaZr_{0.5}Hf_{0.5}Ti_2O_7$, $Gd_2Ti_2O_7$, and $CeTi_2O_6$ is complete.

Research efforts at Los Alamos have focused on establishing synthesis techniques for actinide-bearing minerals and preparation of the calorimetry laboratory. Solid state synthesis techniques are being investigated for the preparation of pyrochlore, $CaAnTi_2O_7$ where An is a actinide, plutonium-doped zircon, $ZrxPu_{1-x}SiO_4$, and plutonium silicate, $PuSiO_4$. X-ray diffraction analysis of the silicate samples revealed considerable sample - container interaction. Alternative container materials will be examined in future synthesis experiments so that high purity minerals can be produced for use in the calorimetry experiments.

Planned Activities

Research at UC Davis will continue with solution calorimetry experiments for $CaHfTi_2O_7$, $CaZr_{0.5}Hf_{0.5}Ti_2O_7$, $Gd_2Ti_2O_7$, and $CeTi_2O_6$. A model for predicting the solution energetics of the actinide(IV) oxides in the calorimetry solvent has been developed. Validation of the model with ThO_2 is expected in the next six months which will allow for the extension of solution calorimetry to other actinide-bearing materials.

Research at Los Alamos will continue with the solid state synthesis of actinide-bearing pyrochlore and silicate minerals, preparation of the calorimetry laboratory, and a series of calorimetric experiments. The calorimetric experiments will include determining the enthalpy of solution of binary actinide oxides, actinide-bearing minerals, and solid solutions of minerals in the calorimetric solvent. Results from the solution calorimetry experiments will be used to calculate the enthalpy of formation of the actinide-bearing minerals (e.g., $CaPuTi_2O_7$) and the enthalpy of mixing in solid solution systems (e.g., $ZrxPu_{1-x}SiO_4$). The thermodynamic data will be used to establish the stability and bonding characteristics of the materials.

Other Access To Information

R.L. Putnam, A. Navrotsky, B.F. Woodfield, J. Boerio-Goates, and J.L. Shapiro, "Thermodynamics of Formation for Zirconolite, $CaZrTi_2O_7$, from T= 298 K to T= 1500 K," submitted to J. Chem. Thermodynamics (1998).

B.F. Woodfield, J. Boerio-Goates, J.L. Shapiro, R.L. Putnam, and A. Navrotsky "Molar Heat Capacity and Thermodynamic Functions of Zirconolite, $CaZrTi_2O_7$," submitted to J. Chem. Thermodynamics (1998).

R. L. Putnam, A. Navrotsky, B. F. Woodfield, J. L. Shapiro, and J. Boerio-Goates, "Heat Capacity, Third Law Entropy, and Formation Energetics of Zirconolite, $CaZrTi_2O_7$," submitted to Proceedings of the100th Annual Meeting of the American Ceramic Society: the International Symposium on Waste Management Technologies in Ceramic and Nuclear Industries (1998).

Development of Nuclear Analysis Capabilities for DOE Waste Management Activities

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Mark D. DeHart, Oak Ridge National Laboratory
Bryan L. Broadhead, Oak Ridge National Laboratory
Calvin M. Hopper, Oak Ridge National Laboratory

Research Objective

The objective of this project is to develop and demonstrate prototypic analysis capabilities that can be used by the nuclear safety analysis practitioners to:

1. demonstrate a more thorough understanding of the underlying physics phenomena that can lead to improved reliability and defensibility of safety evaluations; and
2. optimize operations related to the handling, storage, transportation, and disposal of fissile material and DOE spent fuel.

To address these problems, the project will investigate the implementation of sensitivity and uncertainty methods within existing Monte Carlo codes used for criticality safety analyses, as well as within a new deterministic code that allows specification of arbitrary grids to accurately model the geometry details required in a criticality safety analysis. This capability can facilitate improved estimations of the required subcritical margin and potentially enable the use of a broader range of experiments in the validation process. The new arbitrary-grid radiation transport code will also enable detailed geometric modeling valuable for improved accuracy in application to a myriad of other problems related to waste characterization. Application to these problems will also be explored.

Research Progress and Implications

This report summarizes the progress achieved after only seven months of work on a three-year project. Earlier work[1] at ORNL has used one-dimensional (1-D) deterministic codes to provide a scientific basis for using sensitivity and uncertainty analyses techniques to estimate subcritical margins in safety analyses. This current project is investigating the reliability of sensitivity and uncertainty analysis techniques in the three-dimensional (3-D) Monte Carlo codes typically used for criticality safety analyses. Sensitivity information for a system model is generated via a perturbation theory approach where changes in the system multiplication factor, k-eff, are related to changes in the constituent nuclear data parameters by relationships consisting of the forward and adjoint neutron fluxes. However, in Monte Carlo codes, the angular fluxes needed to obtain sensitivities for certain important reaction types are quite difficult to obtain with the needed accuracy.

Initial studies with Monte Carlo codes have concentrated on using the KENO V.a code of the SCALE code system[2] to compute the sensitivity of k-eff to the bar parameter. This parameter quantifies the number of neutrons generated per fission event and can be a very useful parameter in sensitivity studies; however, angular fluxes are not needed in determination of this parameter sensitivity. A new prototypic code called the Sensitivity Analysis Module for SCALE (SAMS) has been developed to read restart files from forward and adjoint KENO V.a calculations, along with the cross-section data associated with these cases, and then calculate sensitivity profiles (sensitivity as a function of neutron energy) requested by the user. This initial version of SAMS is very limited in the types of problems that can be handled and in the types of sensitivities that can be calculated.

Initial studies using KENO V.a and SAMS indicate that, without modifications, KENO V.a will not produce reliable adjoint solutions for cases that are not well moderated. Thus, as an initial

reference point, low-enriched, well-moderated systems have been investigated. To verify the bar sensitivity capability of SAMS for a thermal system, a test case was modeled using both the 1-D deterministic codes XSDRNPM and KENO V.a. The test case chosen was an unreflected parallelepiped of homogeneous $U(2)F_4$ and paraffin with an H/X ratio of 195.2 and external dimensions of 71.47 cm x 71.47 cm x 94.14 cm. This geometry was explicitly modeled in KENO V.a and was approximated in XSDRNPM as a sphere. The bar sensitivities for ^{235}U and ^{238}U demonstrate excellent agreement between the two sensitivity analyses.

An automated grid-generation scheme has been implemented in the two-dimensional (2-D), arbitrary-grid code NEWT.[3] The goal is to provide the user with an easy-to-use input process that will rapidly and flexibly generate complex geometric models. Grid schemes are generated based on the specification of elementary bodies (initially only cylinders and cuboids) in a problem domain, with user-defined grid refinement parameters. Within this scheme, localized grid refinement is possible to improve geometric detail and accuracy. More advanced grid generation schemes for additional body types and general polynomial surfaces have been conceptualized and studied for potential inclusion in the grid generation logic of NEWT.

An input interface consistent with the specifications typically used by control modules of the SCALE code system has been developed for the application of NEWT in the area of criticality safety. In addition, NEWT is being implemented within the depletion sequence of SCALE. Using the arbitrary-grid capabilities of NEWT, it is possible to obtain accurate 2-D flux distributions which, when used within the depletion sequence, will allow improved characterization of the complicated, heterogeneous fuel assemblies typical of the DOE-owned spent fuel inventory. An operational prototype of this sequence is expected to be complete by the end of FY 1998 and could be used within the DOE/EM program to investigate the adequacy of the spent fuel characterization methods currently obtained only through the application of several simplifying approximations.

Planned Activities

During FY 1998 and 1999 work will be performed to identify and implement techniques and code improvements that will enable full utilization of the sensitivity/uncertainty methodology within 3-D Monte Carlo codes. Also, during this period, a general automated grid generation will be developed and implemented within a SCALE criticality sequence that uses the NEWT code and interfaces with the existing sensitivity/uncertainty analysis module. Extension of NEWT to 3-D will be explored. In FY 2000, these prototypic tools will be used on actual DOE/EM applications to help demonstrate benefits and to understand limitations of the tools and techniques developed under this project. Where possible, enhancements will be made as identified via applications.

Other Access To Information

1. B.L. Broadhead, "Application of Generalized Linear Least-Squares Methodology to Criticality Safety Computations," pp. 234–235 in *Proceedings of the ANS 1997 Winter Meeting and Embedded Topical Meetings*, Albuquerque, New Mexico, November 16–20, 1997.
2. *SCALE: A Modular Code System for Performing Standardized Computer Analyses for Licensing Evaluation*, NUREG/CR-0200, Rev. 5 (ORNL/NUREG/CSD-2/R5), Vols. I–III (March 1997). Available from Radiation Safety Information Computational Center, Oak Ridge National Laboratory, as CCC-545.
3. M.D. DeHart, "An Advanced Deterministic Method for Spent Fuel Criticality Safety Analysis," in *Proceedings of the 1998 ANS Annual Meeting and Embedded Topical Meeting*, Nashville, Tennessee, June 7–11, 1998

Determination of Transmutation Effects in Crystalline Waste Forms

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Nancy J. Hess, Pacific Northwest National Laboratory
Jeffery A. Fortner, Argonne National Laboratory
Edgar C. Buck, Argonne National Laboratory

Research Objective

To determine the effect of transmutation of ^{137}Cs to ^{137}Ba on crystalline waste forms by examining old samples of pollucite ($CsAlSi_2O_6$) in stainless steel capsules.

Research Progress and Implications

In this report, we summarize the research that has taken place during the second year of the 3-year project. This project is being carried out at Pacific Northwest National Laboratory and Argonne National Laboratory.

The original intent in this project was to use high-energy EXAFS to obtain information on the chemical state of the ^{137}Ba in pollucite without opening the stainless steel capsules. Using this approach, we hoped to avoid changing the chemical state of the ^{137}Ba. To evaluate the extent to which high-energy EXAFS data can be interpreted, we analyzed a number of Cs and Ba standards in addition to Ba-doped pollucite samples. The standards included a variety of structures from simple oxides and halides to titanates and silicates. While the EXAFS signal from the simple oxides and halides were low in amplitude the analysis of the EXAFS and the Fourier transforms resulted in reasonable data. We obtained extremely weak EXAFS signals from the more complex silicates and titanates with distant first neighbor atoms. In addition, the amplitudes of the Cs K-edge EXAFS are

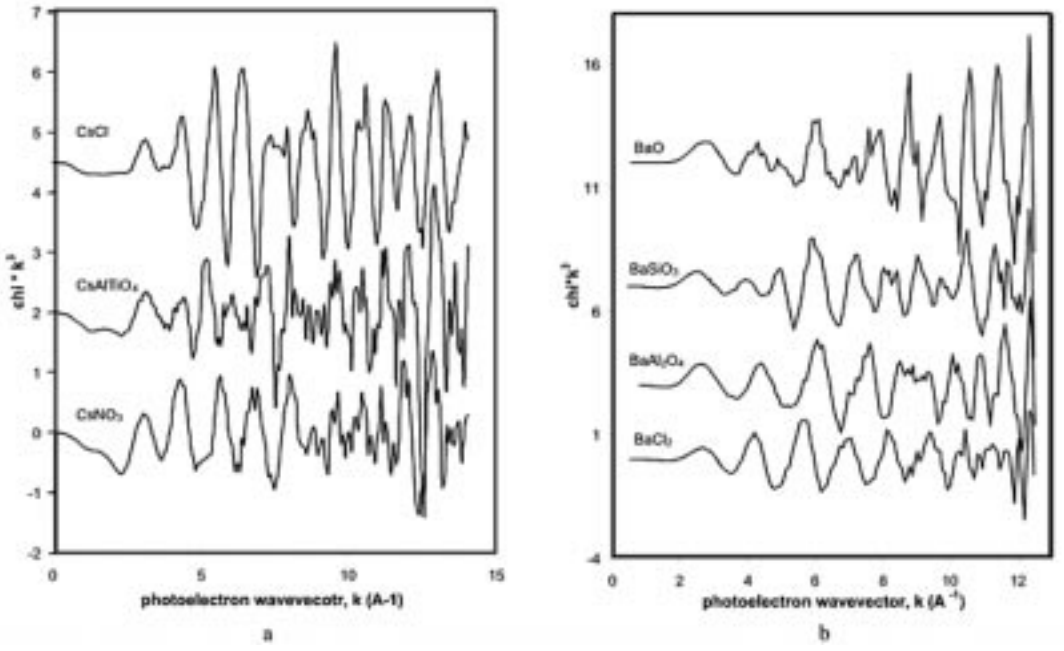

Figure 1. Cesium (a) and Barium (b) K-edge EXAFS.

about half as intense as the corresponding Ba K-edge EXAFS (Figure 1). Several factors may have contributed to the apparent differences between the Cs and Ba K-edge data, such as core-hole lifetime broadening, weak photoelectron backscatters, and low charge density of the large low-valence cations. Also, long interatomic distances appear as low frequency oscillations in the XAS and these features could have been inadvertently removed when we tried to extract the EXAFS. Artifacts that have no possible structural origin often dominated the Fourier transforms from these compounds. A number of signal processing techniques were employed in an attempt to minimize these artifacts but they generally resulted in severe distortions of the weak EXAFS signal.

Regardless of the specific origin, these factors reduce the extent to which the Cs K-edge EXAFS data can be interpreted. We conclude that Cs and Ba K-edge EXAFS can be used successfully for materials where the structure is relatively simple and the material is well ordered. However, in materials with low atomic number backscatterers and low symmetry such as pollucite, it is not possible to determine the effects of ^{137}Cs beta decay and transmutation on the pollucite structure. However, one can reasonably hope to identify the presence of metallic Ba clusters or BaO, if either are the result of transmutation.

To overcome the shortcomings with the high-energy EXAFS, we have explored the use of nuclear magnetic resonance (NMR) spectroscopy to examine the local structure of the cesium in some laboratory-prepared pollucite. Small quantities, typical of what we expect to recover from the sealed capsules, proved to be sufficient material to obtain spectra with both magic-angle spinning and static NMR techniques (Figure 2). The chemical shift is expected to be sensitive to local structure and to disorder. We expect to prepare a sample from the ^{137}Cs pollucite when we open a capsule.

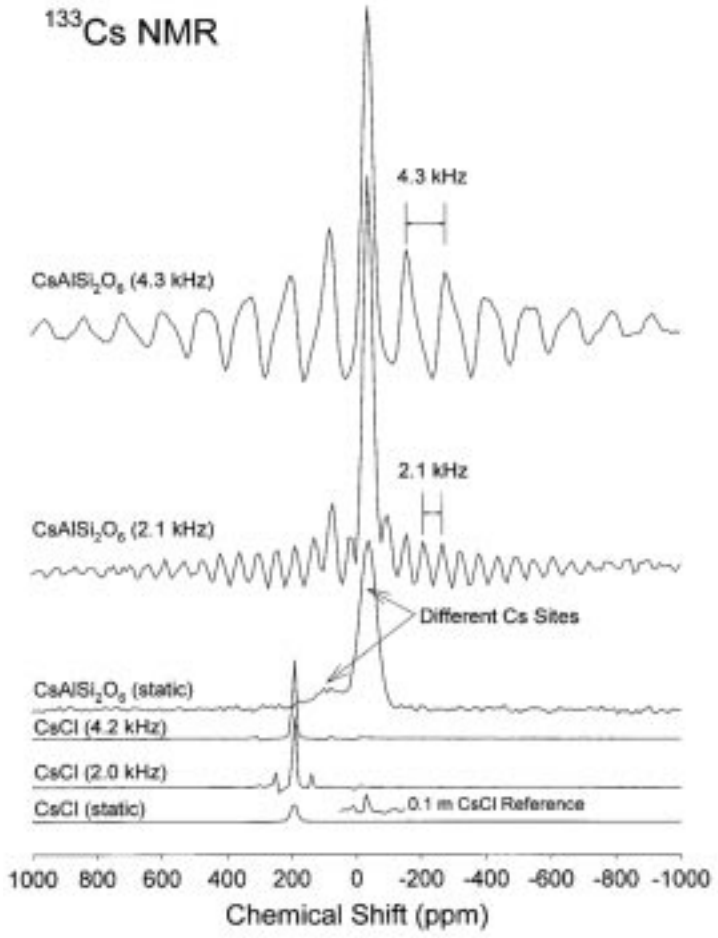

Figure 2. Nuclear Magnetic Resonance Spectra From Cs-Containing Materials Sample (Above) Along With Reference Materials. The Spinning Frequency Of Magic Angle NMR Is Indicated In Parentheses.

Planned Activities

We have prepared documentation for a safety review of a procedure for opening a capsule of pollucite containing up to 80 mCi of ^{137}Cs. We anticipate opening the first capsule of radioactive pollucite in July 1998. The material will be loaded into sample cells for EXAFS, NMR, and Analytical Electron Microscopy.

Miniature Nuclear Magnetic Resonance Spectrometer for In-Situ and In-Process Analysis and Monitoring

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Alan D. Feinerman, University of Illinois at Chicago

Research Objective

The purpose of this research project is to develop a miniature Nuclear Magnetic Resonance (NMR) spectrometer. This analytical instrument would potentially be used for in-situ, in-field and in-process monitoring, characterization and identification of various chemical compounds. The intended spectral resolution of the NMR spectrometer is better than 0.1 ppm (parts per million). The development of the miniature NMR spectrometer will rely, in part, on the microfabrication technology that includes photolithography, chemical etching, thin film processing and other techniques originally developed in microelectronics. Miniaturization of the NMR spectrometer will involve the miniaturization of the inductive NMR probes used to pick-up the NMR signals. It will also involve integration of the probe, sample holder and magnetic field correction (shimming) coils into a single miniature system. Lastly, it will involve the development of a hand-held permanent magnet capable of creating magnetic field of over 1 Tesla with uniformity of about 1 part per million over the extent of the sample. The advantage of the developed instrument will not only be its portability, but also its ability to handle nono-liter quantities of fluids.

Research Progress and Implications

As of today, the following tasks have been completed.

1) Scaled versions (800 micron diameter) of the NMR inductive probes have been designed, fabricated and tested for their radio frequency properties. The resulting probe design, which can be called a scroll coil, has been found to be suitable for further miniaturization and compatible with the existing microfabrication technology. In addition tests and analysis indicate and this design will also provide higher sensitivity to NMR signals per unit volume of the sample than other proposed miniature NMR probes. Analysis and tests of the scroll coil design revealed a surprising fact that the sensitivity of the scroll coil is much better when the conductor thickness is smaller than the conductor skin depth. This result defies the conventional rules of NMR probe design which prescribe that conductors should be thicker than their own skin depth.
2) As samples and NMR probes become smaller, the problem of the NMR spectrum dispersion caused by the mismatch in the magnetic susceptibility of the sample and its surroundings becomes more pronounced. A method and a computer code for numerical modeling of the NMR spectrum dispersion has been developed. Upper bounds on the errors in the spectrum

calculation have been derived. The developed numerical techniques have been applied to design NMR probes that introduce as little distortion as possible to the NMR spectrum. These designs rely on passive shimming (magnetic field correction) by specially patterned parts of the coil.

3) Initial evaluation of a commercially available permanent magnet (from Drexel Corporation) capable of delivering a 2 Tesla field has been carried out using numerical modeling.

Planned Activities

1) Complete miniature NMR probe design fabrication and testing by 12/98. This involves fabricating double layer films consisting of dielectric (polyimide) and conductor (copper). The challenge is to make conductor thickness between 2.5 and 5 microns uniformly. Another step needed for the completion of the NMR probe is the improvement of the developed rolling technique allowing to reduce the probe diameter down to 100 microns. The final test of the probe should be to obtain NMR spectrum in a conventional spectrometer.
2) Complete evaluation and design of the permanent magnet by 5/99. This involves, most likely, modifying the magnet available from the Drexel Corporation.
3) Evaluate stability of the magnet and design temperature stabilizing system around it by 12/99.
4) Design the magnetic field correction (shimming) coils to be integrated into one system with the NMR probe by 9/99. Fabricate and test these shimming coils together with the NMR probe by 5/2000.
5) Put together the miniature NMR system including NMR probe, sample holder and shimming coil assembly and the permanent magnet with the temperature stabilizing system by 9/2000. Testing of the miniature NMR system should be completed before 12/2000.

Remedial Action

Research Program to Determine Redox Properties and Their Effects on Speciation and Mobility of Pu in DOE Wastes

Gregory R. Choppin, Florida State University

Dhanpat Rai, Pacific Northwest National Laboratory

Research Objective

The goal of our research is to develop data to allow successful modeling of the effects of redox chemicals present in Hanford waste tanks on the oxidation state and chemical speciation of plutonium in the wastes.

Research Progress and Implications

As of May 1998, scoping experiments on PuO^{2+} in a solution of 1.0 M NaCl and pH 8 in the dark showed no reduction of PuO^{2+} concentration over a week nor was reduction observed when this experiment was repeated with 10^{-5} M H_2O_2. Reduction was observed over hours/days as the H_2O_2 concentration was raised above 10^{-3} M. The rate of reduction in the dark was measured at pcH = 8, 1.0 M (NaCl) for $[H_2O_2] = 10^{-2}$ to 4×10^{-2} and $[PuO^{2+}] = 1.2 \times 10^{-10}$ to 3.5×10^{-10} M and first order kinetics observed. From the rate constants, we calculate for $[H_2O_2] = 10^{-2}$ M and $[PuO^{2+}] = 10^{-6}$ M, a half life of reduction in the dark of 0.06 min and for $[H_2O_2] = 10^{-6}$ M, $[PuO^{2+}] = 10^{-6}$ M, of 10 hr. These data indicate that radiolytic production of H_2O_2 in the wet tank wastes would serve to reduce PuO^{2+} (and PuO_2^{2+}) to Pu(IV), thereby reducing the concentration of dissolved Pu due to the strong hydrolytic tendency of the Pu(IV).

The oxidation of Pu(IV) by NaOCl is also being investigated. As of May, 1998, the methodology to measure the oxidation state speciation at tracer Pu(IV) concentrations has been developed and scoping experiments conducted. At pcH 4.7, I = 1.0 M (NaCl), [Pu(IV)] = 10-10 M and [NaOCl] = 10^{-5} to 10^{-3} M, no oxidation (i.e., PuO_2^{2+}) has been observed. Experiments are now underway at pcH = 8.

To understand the role of complexation by the strong organic ligand in the tank wastes in the redox speciation of Pu, we are measuring the stability constant of Pu(IV) with EDTA. Attempts to use arsenazo (III) as a chromophoric competing ligand were unsuccessful and as of May, 1998, we are studying competition experiments of Pu(IV) and Fe(III) with EDTA by absorption spectrophotometry. A value of log 101 = 24.0 ± 0.1 has been obtained for I = 1.0 m (NaCl).

Planned Activities

In FY 98, experiments on PuO^{2+} reduction by H_2O_2 will be conducted at varying pH values to determine the influence of the H^+ and OH^- concentration. These studies will be continued in FY 99 at 0.4 m and 4.0 m (NaCl) ionic strengths. This should allow calculation of the rates of reduction of Pu(V) under conditions relevant for the tank wastes and for environmental systems. The NaOCl studies in FY 98 will measure pcH, NaOCl and Pu(IV) concentration dependencies to develop a useful rate equation. Again, the experiments will cover 0.4, 1.0 and 4.0 m (NaCl) media in FY 99. The measurements of the stability constants of Pu(IV)EDTA will be performed at I = 0.3 m and I = 3 m (NaCl) during the remainder of FY 98. We plan to measure the FeEDTA- constant under these conditions in FY 99. The research in that year will focus on similar measurements for the formation of Pu(IV)DTPA-. These values will allow modeling of the role of EDTA and DTPA in Pu speciation in the tank wastes.

In the remainder of FY 98 and FY 99, experiments will also be conducted to determine the effects of Fe(II) and ferridoxin (common to electron transport system in anaerobic bacteria) on the oxidation states of Pu. Specifically, effects of pH, concentrations of $FeCl_2$, $FeClO_4$, and ferridoxin will be evaluated on the solubility of PuO_2(am). Total concentrations and oxidation states of aqueous Pu and Fe, along with changes in solid phases as a function of time, will be monitored. The oxidation states will be monitored using a combination of solvent extraction, and spectrophotometric and x-ray absorption spectroscopies. The results will provide information on the expected dominant Pu species in environments containing Fe(II) and microbially produced reducing agents.

Speciation and Structural Characterization of Plutonium and Actinide-Organic Complexes in Surface and Groundwaters

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Research Objective

Our proposed research is designed to study the association of actinides with dissolved organic complexes in subsurface waters. This study expands considerably on prior work due to the combination of Pu oxidation studies (for Pu speciation/chemical reactivity information), Pu isotope ratio work (for Pu source function information), and the detailed characterization of organic matter in size-fractionated groundwater samples. We have postulated that actinide associations with organic matter may be enhanced due to colloidal biopolymers.

Research Progress and Implications

This report summarizes work completed after less than 2 years of a 3-year project. Activities thus far have included: 1) the development of sampling techniques to minimize contamination and artifact formation, 2) the separation of Pu isotopes by oxidation state in groundwater, 3) the development of techniques for the separation and identification of organic constituents from natural waters, 4) a study of background Pu and organic carbon concentrations at the proposed study sites, and 5) field work at the Savannah River site (SRS).

Sampling

Our proposed research calls for field work at the Savannah River and Hanford Sites (SRS and HS, respectively). Towards this end, we have established protocols for the sampling and analyses of organics and actindes in groundwaters using ultra-clean (fg level) cross-flow filtration (CFF) techniques suitable for thermal ionization mass spectrometric (TIMS) analysis of Pu. A series of tests have been completed and the results have shown that no Pu contamination from the CFF system was observable as long as the system was rigorously cleaned with acid, base and nano-pure water. We have also processed samples from a fresh water pond in Woods Hole, MA, from the groundwater in Falmouth, MA and from the Gulf of Maine (GOM) in order to test blank conditions

in the field, to determine CFF mass balances, and to estimate the Pu colloidal association and isotopic ratio in these contrasting geochemical environments. Our CFF mass balance was generally 100 $\pm$10 % for both ^{239}Pu and ^{240}Pu (Table 1). CFF is known to be prone to both sorptive losses and contamination effects, hence these results are encouraging for the success of the project because CFF will be the major sampling tool we will use to study natural Pu-organic complexes. Also shown in the table are the size fractionated Pu data. In seawater, the majority of Pu was found in the low molecular fraction (<1 kD). Colloidal Pu varied from 8 % of the total in surface waters to <1% in the deepest (250m) seawater sample. In contrast, in a freshwater pond at Woods Hole, all of the Pu was associated with the high molecular weight fraction, most likely due to complexation with organic material. In the groundwater in Falmouth, colloidal Pu represented 57% of the total Pu. These results suggest that the association of Pu with colloidal organic material is highly variable, depending presumably upon the speciation of Pu and the quantity and quality of organic matter in a given aqueous sample.

	Dissolved (< 1 kD)		Colloidal (1 kD - 1 µm)		Particulate (> 1 µm)		CFF Recovery
	dpm/1000kg	% of Total	dpm/1000kg	% of Total	dpm/1000kg	% of Total	(%)
GOM (1m)	0.2205	92.0	0.0099	4.1	0.0094	3.9	99
GOM (15 m)	0.1462	58.5	0.0206	8.2	0.0832	33.3	99
GOM (37m)	0.2106	85.7	0.0165	6.7	0.0187	7.6	87
GOM (65 m)	0.3492	92.1	0.0149	3.9	0.0152	4.0	110
GOM (200 m)	0.4442	88.3	0.0142	2.8	0.0447	8.9	103
GOM (250 m)	0.4512	85.6	0.0003	0.1	0.0758	14.4	96
Nobska Pond	0.04259	0.20	21.3544	99.8	N/A	N/A	110
Falmouth groundwater	0.00105	10.1	0.00592	57.1	0.00341	32.9	71

Preliminary results from the SRS and HS

We collected a suite of samples from SRS and HS for preliminary analyses of total actinide levels and Pu isotope ratio work (in collaboration with the Jim Kelley and John Wacker at PNNL). The ^{240}Pu/^{239}Pu atom ratio in a sample taken from the 100-K area at HS was 0.0498, indicating a local Pu source in this area (global fallout ^{240}Pu/^{239}Pu atom ratio avg. = 0.18). At area F at SRS, ^{240}Pu/^{239}Pu ratios ranged from 3.9 to 0.18, signifying various sources at this one site. The excessively high ratios may be related to the decay of Cm-244 and Cm-243 from wastes.

Organic analyses

CFF organic matter samples collected locally are being used to develop methodologies for sample fractionation and biopolymer identification. We have found that the major organic constituents of our water sample are biopolymers similar in composition to those we have previously identified in seawater. Given that >80% of the dissolved Pu is in this fraction, this result supports our original hypothesis that biopolymeric rather than humic substances may account for a large fraction of actinide-organic matter associations. Specifically, 60% of the carbon in our sample is bound in a mixture of structurally related acyl-polysaccharides. We have made a preliminary investigation of polysaccharide stereochemistry, and are presently conducting analyses of the monosaccharide composition and linkage patterns. In parallel, we are testing chromatographic procedures in an effort to develop protocols to further purify the mixture for more comprehensive spectrometric analyses.

About 35% of our sample is made up of dissolved proteins. We have made a preliminary characterization of these proteins, and we are preparing to make further analyses of protein amino acids and specific components by SDS-PAGE and similar techniques. Finally, only 5% of the carbon in our sample is made up of what are traditionally classified as humic material. NMR spectrometric analyses of this fraction shows a high degree of aromatic character, but a significant acylpolysaccharide component as well. It may be that the humic substances in our sample are derived

from the acyl-polysaccharides described above, or that the humic substances are difficult to purify in the presence of high relative concentrations acyl-polysaccharides.

Comprehensive sampling activity at SRS (April 1998)

Field sampling for at SRS was completed in April 1998 at 8 monitoring wells in F area.

Planned Activities

We are planning to sample at HS this Summer or early Fall. In the lab, the large suite of samples (> 200) from SRS are being processed both for organic and Pu isotopes in the size fractionated samples.

Other Access To Information

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Plutonium Speciation, Solubilization, and Migration in Soils

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Research Objective

The DOE is currently conducting cleanup activities at its nuclear weapons development sites, many of which have accumulated plutonium in soils for 50 years. To properly control Pu migration in soils within Federal sites and onto public lands, better evaluate the public risk, and design effective remediation strategies, a fundamental understanding of Pu speciation, transport, and release mechanisms is needed. Key scientific goals include: determine Pu concentrations and speciation at a contaminated DOE site; study the formation, stability, and structural and spectroscopic features of environmentally relevant Pu (III, IV, and V) species; determine the mechanism of interaction between Pu and Mn/Fe minerals and the potential release of Pu via redox cycling; and model the environmental behavior of plutonium.

Research Progress and Implications

This report summarizes work after seven months of a three-year project. In the first year of this project we are focusing on the origin, speciation, and mobility of plutonium at the Rocky Flats Environmental Test Site (RFETS).

We have reviewed detailed thermal ionization mass spectrometry (TIMS) measurements and resultant $^{240}Pu/^{239}Pu$ atom ratios determined for soil samples collected in the RFETS area and samples collected at locations in Colorado that are believed to be representative of global fallout. These studies were performed to investigate potential migration within and releases from the RFETS site

due to the fires and other events of the 1950s and 1960s and potential releases from the area 903 pad in the late 1970s. Non-fallout isotopic ratios are localized directly east of the site, with only slight divergence north and south of the site—contradicting previous suspicions of long-range contamination from RFETS in the north/south direction. These data allow us to put actinide processes in context regionally and better interpret extensive information collected on site where soil and watershed contamination is much higher. As detailed characterization of the microscopic and molecular state of Pu constituents develops, this context will be essential for remediation and treatment activities.

We have also received extensive data from the site for radiochemical activities in surface water. These data are the basis for evaluating the validity of particulate transport models used by the site, and coupled behavior of ^{241}Am and $^{239/240}$Pu. Over most of the actinide concentration range, Am and Pu activities are roughly correlated, consistent with a particulate transport model. However, at the lowest activities the relative activity of Am spreads toward higher values. Three possible mechanisms have been identified: mixing with contaminant source material enriched in Am, variation in the relative mobilities of Am and Pu, and contribution of natural Th to the low level counting results. Further evaluation is critical to coupling the detailed chemical and physical model sought by this project to remediation and treatment actions at Rocky Flats and other sites contaminated with low levels of actinides.

Chemical analyses from the database for 1992 through 1994 for pond C-2, a main drainage pond at RFETS, include constituents important for understanding the geochemistry of natural waters, including bicarbonate, chloride, sodium, sulfate, sulfide, and some metals. Radiochemical analyses were conducted almost monthly between 1992 and 1995. Seasonal variation in the plutonium concentrations in Pond C-2 is observed for 1992, 1993 and 1994. To evaluate whether these seasonal patterns are related to colloidal plutonium, total suspended solids (TSS) and plutonium are compared. The 1994 TSS data exhibit a pattern that correlates with plutonium. This relationship suggests that colloidal plutonium may, in part, cause the observed seasonal fluctuations. Sulfur and manganese exhibit trends in C-2 Pond water that correlate with the plutonium pattern, suggesting that geochemical processes, in addition to colloid formation, are contributing to the observed variation in soluble plutonium. The most prominent changes observed in pond C-2 are temperature, from 27.4 to 4.5ºC, and dissolved oxygen content, from 0.5 to 7.8 mg/L. Given the water analysis, including redox sensitive species, the Eh (redox potential) of the system varies from -0.278 V and +0.750 V. (The potential dictates the oxidation state(s) of plutonium which are stable, and thus controls the solubility of plutonium.) These variations and simple geochemical models were used to attempt to determine the processes occurring within Pond C-2. The observed trends in sulfate and plutonium are duplicated; however, the models do not yet duplicate the magnitude of change observed for plutonium and sulfate or the pattern observed for manganese.

We have received and are analyzing a number of soil and water samples from the RFETS. We attempted to determine the oxidation state of the plutonium in a sample from a core from pond B-1 using X-ray absorption near-edge spectroscopy (XANES). Unfortunately, the sample has a relatively high concentration of Zr or another element which has an absorption edge very close in energy to the Pu edge. (Zirconium has an absorption edge at 17999.35 eV; plutonium species have absorption edges of 18056, 18058, 18060 and 18061 eV for Pu III-VI, respectively). We did not observe an absorption edge corresponding to the Pu in the soil sample. We may attempt to remeasure the X-ray absorption after a pre-concentration step and using another absorption edge for plutonium which does not have the same interference problem. For comparison, we recently measured the XANES spectrum of 3.2 mg/g or 372 nCi ^{239}Pu sorbed onto smectite. The spectrum for this sample shows two edge features, one at 18000 eV and the other at ~18060 eV, suggesting the presence of zirconium and Pu(IV) or Pu(V). The observation of the Pu edge for this mineral sample is encouraging since we have received soil samples which have comparable Pu concentrations.

Planned Activities

This year we will continue RFETS related experiments and geochemical modeling. We will determine the overall Pu content and isotopic ratios for sediments and waters from RFETS. We will characterize the Pu in soil samples by determining morphology, degree of mineralization, and bulk distribution

between types of phases using a combination of techniques. Sequential filtration studies may indicate the size distribution of host particle and allow us to determine if Pu is migrating via resuspended particles or via redox transformation to different chemical species. We will attempt to determine the overall Pu oxidation state. We will continue to model the chemistry of ponds at RFETS and attempt to explain the seasonal variations in soluble Pu. To obtain more precise data for the geochemical modelling we will work with the site to measure the redox potential in the ponds.

In the following years we will continue to characterize the Pu in RFETS soils and perform laboratory studies on Pu carbonato and hydroxo species, both as pure systems and interacting with Mn ions and oxides. We anticipate that our soils characterization studies from the first year will confirm our choice of the Pu(III, IV, and V) single carbonate and Pu(III and IV) hydroxide systems and will allow us to refine our targets for fundamental studies. Obtaining characteristic spectra and determining the stability and properties of the species will not only provide spectroscopic and thermodynamic data to compare with environmental samples, but also allow us to unravel the equilibrium constants of important actinide systems. Investigating the Mn/Pu redox cycle and Pu sorption mechanisms and geochemical of Pu will further improve our understanding of the complex environmental behavior of Pu.

Mechanisms, Chemistry, and Kinetics of Anaerobic Biodegradation of Cis-Dichloroethylene and Vinyl Chloride

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Research Objective

The objectives of this study are to: (1) determine the biochemical pathways for reductive dehalogenation of cis-1,2-dichloroethene (cDCE) and vinyl chloride (VC), including identification of the enzymes involved, (2) determine the chemical requirements, especially the type and quantity of electron donors needed by the microorganisms for reductive dehalogenation, and (3) evaluate the kinetics of the process with respect to the concentration of both the electron donors and the electron acceptors (cDCE and VC).

Research Progress and Implications

Progress has been made under each of the three primary objectives. One manuscript related to the first objective has been published. Manuscripts related to the other two objectives have been submitted for publication. Findings related to the three objectives are summarized in the following.

Objective One - Biochemical Pathways and Enzymes

Reductive dehalogenation of VC was studied with an anaerobic mixed culture enriched on VC. In growth experiments, ethene formation from VC increased exponentially at a rate of about 0.019 h^{-1}. Reductive VC dehalogenation was measured in vitro using cell-free extracts of the mixed culture. The apparent K_m for VC was determined to be about 76 μM; V_{max} was about 28 $nmol \cdot min^{-1} \cdot [mg\ protein]^{-1}$. The VC dehalogenating activity was membrane-associated. Propyl iodide had an inhibitory effect on the VC dehalogenating activity in the in vitro assay. However, this

inhibition could not be reversed by illumination as is generally the case when vitamin B-12 is the transforming factor involved. Cell-free extracts also catalyzed the reductive dehalogenation of cDCE and, at a much lower rate, trichloroethene (TCE). Tetrachloroethene (PCE) was not transformed. The results indicate that the VC dehalogenating microorganism(s) in the enrichment culture could also dehalogenate cDCE, but not the more chlorinated ethenes. Thus, the reductive dehalogenation by this culture is different from previously reported reductive dehalogenations of PCE and TCE.

Objective Two - Chemical Requirements

A continuously stirred tank reactor (CSTR) was used to develop a PCE-dehalogenating enrichment culture, and was originally seeded with sediment from a PCE-contaminated groundwater aquifer in Victoria, Texas, where complete reduction to ethene was occurring following addition of benzoate to the groundwater. A study using several potential electron donors, including benzoate, sucrose, lactate, ethanol, and acetate indicated most complete conversion of PCE to ethene was obtained with benzoate. Benzoate was thus selected as the donor and was fed at a constant concentration of 1.7 mM along with 1.0 mM PCE to provide a 36 day detention time. Near complete conversion of PCE to ethene was obtained. A mass balance indicated 70 % of the benzoate electron equivalents were converted to acetate, 13 % to methane, 9 % to dehalogenation, and 4 % to biomass.

Anaerobically, one mole benzoate is theoretically fermented to 3 moles of acetate and 3 moles of hydrogen. Our laboratory study results indicate hydrogen is the major electron donor for cDCE and VC dehalogenation. Batch studies were conducted to evaluate the competitors for available hydrogen, and indicated these were homoacetogens, methanogens, and dehalogenators. At higher hydrogen concentrations (> 400 nM), conversion to acetate by acetogens dominated the reaction. At hydrogen concentration somewhat above 12 nM, methanogens were highly competitive. However, with hydrogen concentration between 2 and 11 nM, dehalogenation was the most competitive process. Low hydrogen concentrations that favored dehalogenation could be maintained with the CSTR, but were difficult to obtain with batch donor addition. This suggests a useful approach for reductive dehalogenation of PCE.

Objective Three - Process Kinetics

Preliminary studies suggest the affinity constant for hydrogen used in dehalogenation of cDCE and VC to be about 20 nM, which is consistent with values provided by others. Studies on the affinity constants (K_s) for the chlorinated ethenes themselves, while serving as electron acceptors, indicate the value for PCE (0.06 μM) is much lower than that for TCE (1.4 μM), cDCE (3.4 μM), and VC (2.7 μM). The maximum rate for PCE dehalogenation was about 2 $nmol \cdot min^{-1} \cdot [mg\ protein]^{-1}$. That for TCE was about the same, while the values for cDCE and VC were about one-fifth of the value for PCE. These rates, which are based upon total population concentration rather than the compound specific population, are low compared with that for the VC enrichment noted under Objective One where the culture was much more enriched for the specific organism of interest. The relative rates, however, do fit within the general observation that PCE and TCE dehalogenations are much faster than for cDCE and VC.

Another observation made was the particular toxicity to methanogens and dehalogenators of cDCE. A phenomenon was found where cDCE could be dehalogenated with initial concentrations as high as 400 μM as long as the microorganism population started at a sufficiently high concentration so that dehalogenation was complete within a few days. However, at lower population levels where dehalogenation may take longer than about 10 days, the dehalogenation slowed down and eventually stopped. Further studies indicated that inhibition with high cDCE concentration was a time dependent factor. The inhibition resulted in slow organism death. A more detailed study of this phenomenon indicated that cDCE concentration must be below about 20 μM for inhibition to be absent to small initial dehalogenating populations. This is an important finding for groundwater systems where concentrations of cDCE are often higher than this level for extended periods of time. Initial studies with high cDCE and population concentrations missed this phenomena.

Planned Activities

Research under all three objectives is continuing. Under objective one, efforts are being made to purify the dehalogenating enzymes. Under objective two, studies are being conducted to find ways to increase the efficiency of electron donor utilization for dehalogenation. Under phase three, further efforts are being made to quantify the kinetics of dehalogenation.

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Complete Detoxification of Short Chain Chlorinated Aliphatic Compounds: Isolation of Halorespiring Organisms and Biochemical Studies of the Dehalogenating Enzyme Systems

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Research Objective

Widespread use and careless handling, storage and disposal practices, have lead to the dissemination of chlorinated short chain aliphatics into groundwater systems. These compounds are toxic and the presence of chlorinated ethenes and chlorinated propanes in the environment is of public concern. Halorespiration is a newly recognized anaerobic process by which certain bacteria use chlorinated compounds as terminal electron acceptors in their energy metabolism. In contrast to co-metabolic dechlorination, which is fortuitous, slow, and without benefit to the organisms, halorespiration, characterized by high dechlorination rates, is a specific metabolic process beneficial to the organism. Our goals are to isolate and characterize organisms which use chlorinated ethenes (including tetrachloroethene [PCE], trichloroethene [TCE], cis-dichloroethene [cis-DCE], and vinyl chloride [VC], or 1,2-dichloropropane [1,2-D]) as electron acceptors in their energy metabolism. Better understanding of the physiology and phylogeny of the halorespiring organisms as well as the biochemistry of the dehalogenating enzyme systems, will greatly enhance our knowledge of how these organisms can successfully be employed in the bioremediation of contaminated sites.

Research Progress and Implications

This report summarizes the results of 1.5 years of a 2-year project.

Anaerobic microcosms were established using a variety of geographically distinct sediments. In several microcosms complete dechlorination of PCE to ethene (ETH), and 1,2-D to propene was observed. Upon subsequent transfers to anaerobic medium, four sediment-free, methanogenic enrichment cultures were obtained that dechlorinated PCE to ETH, and two cultures that dechlorinated 1,2-D to propene. 2-Bromoethanesulfonate (BES), a well known inhibitor of methanogens, did not

inhibit the dechlorination of 1,2-D to propene or the dechlorination of PCE to cis-DCE. However, the complete dechlorination of PCE to VC and ETH was severely inhibited. We could also show that BES inhibited the dechlorination of chloroethenes in cultures without methanogens. Therefore, BES should not be used to attribute dechlorination activities to methanogens.

The non-methanogenic cultures obtained after the BES treatment were subsequently transferred to medium without BES, and complete dechlorination of PCE to ETH occurred as in the original microcosms. Subcultures were further enriched with PCE, cis-DCE, VC, or 1,2-D as the only available electron acceptor and with acetate, or acetate plus hydrogen as the only available electron donor(s). To date, these cultures have undergone over 30 transfers. Three cultures that had originally dechlorinated PCE to ETH, but were then enriched with cis-DCE or VC, lost their ability to dechlorinate PCE. This finding indicates that different populations are involved in the complete dechlorination of PCE to ETH in these cultures. Interestingly, one sediment yielded cultures that maintained their ability to dechlorinate PCE even after enrichment with cis-DCE or VC. Using molecular tools (16S rDNA targeted PCR, TA cloning of 16S rDNA genes, ARDRA analysis and sequencing) we showed that the PCE-dechlorinating culture consisted of two distinct populations. One of them was isolated in pure culture yet showed no dechlorinating activity, indicating that the other population, or the interaction of the two, was responsible for the complete dechlorination of PCE to ETH in the co-culture. Hydrogen was the only electron donor shown to support dechlorination. We are currently focused on isolating this interesting dechlorinator, and on the taxonomic characterization of both members of the consortium.

Reductive dechlorination of cis-DCE or VC to ETH in the four cis-DCE/VC enrichment cultures unable to dechlorinate PCE, was supported by a variety of electron donors, including hydrogen. In a bicarbonate-buffered medium in the presence of cis-DCE or VC as electron acceptor, hydrogen was consumed below concentrations of 0.5 ppmv. In contrast, the same cultures consumed hydrogen to threshold concentrations around 300 ppmv in the absence of the chlorinated ethene. These findings suggest that both cis-DCE and VC can be used as terminal electron acceptors by at least one population in our highly enriched cultures.

To date we have isolated two pure cultures of PCE dechlorinating organisms from these enrichments. One isolate, a strictly anaerobic organism designated strain BB1, dechlorinated PCE to cis-DCE using acetate, lactate, or pyruvate, but not hydrogen or formate, as electron donors. This is an important observation since it is generally believed that hydrogen is the ultimate electron donor supporting chlororespiration in anaerobic environments. Phylogenetic analysis showed that this organism belongs to the genus Desulfuromonas and its closest relative is another PCE to cis-DCE dechlorinating organism, Desulfuromonas ethenica strain TTB4. However, in addition to several key physiological features, strain BB1's16S rDNA sequence is 5% different from the sequence of strain TTB4 indicating that strain BB1 is a different species. Strain BB1's ability to grow by chlororespiration was confirmed by showing PCE dependent growth with acetate, and by determining the fe value. The fe value describes the fraction of electrons transferred from the electron donor (acetate) to the electron acceptor (PCE). Strain BB1 revealed an fe value of 0.66 indicating that 66% of the electrons from acetate were consumed in the reductive dechlorination of PCE to cis-DCE. Furthermore, we optimized the culture conditions to obtain sufficient cell material to assess PCE dechlorinating activity in cell-free systems. A test system to measure PCE dechlorination using gas chromatography was developed. The reductive dechlorination of PCE and TCE to cis-DCE could be measured with reduced methyl viologen as the electron donor. Dechlorination activity was membrane fraction associated with less than 1% of the total activity remaining in the soluble protein fraction, which suggested that the dechlorinating enzyme system is membrane-bound. The membrane-bound reductive dechlorinase could be solubilized with 1% Triton X-100, and up to 80% of the total initial activity could be recovered in the solubilized fraction.

The other isolate that dechlorinated PCE to TCE was designated strain Viet1. This strictly anaerobic organism was identified as a new member of the genus Desulfitobacterium. Strain Viet1 grew well on pyruvate, and a variety of electron donors, including hydrogen and formate, supported dechlorination. Therefore, sufficient cell material for the investigation of cell-free dechlorinating activity was available. The capacity for chlororespiration was confirmed by hydrogen threshold measurement, fe value determination, and PCE dependent growth.

Two microcosms which were enriched with 1,2-D, yielded sediment-free, nonmethanogenic cultures that completely dechlorinated 1,2-D to propene. These could be indefinitely transferred to mineral salts medium containing acetate as a carbon source and hydrogen as the electron donor. Hydrogen threshold measurements confirmed that chlororespiring organisms were responsible for the conversion of 1,2-D to propene. ARDRA analysis of a clone library from one of the enrichment cultures showed seven different patterns. Partial sequence analysis of the cloned 16S rDNA genes revealed that six of the seven clones had identical sequences with only one distinct sequence. We are currently analyzing the complete 16S rDNA sequences in order to determine the phylogenetic relationships of the organisms. This will permit the development of an efficient isolation procedure for the dechlorinating populations.

Planned Activities

(1) Determination of fe values and hydrogen thresholds to confirm the presence of chlororespiring organisms in all cultures. This ongoing work will be completed within the next 2 months.
(2) Phylogenetic analysis of the highly enriched mixed cultures that dechlorinate cis-DCE, VC, or 1,2-D, and the PCE to ETH dechlorinating co-culture. This work is in progress and will be completed within the next 3 months. The goal is to purify and identify the dechlorinating populations.
(3) Purification of the PCE/TCE reductive dechlorinase from strain BB1, and the PCE reductive dechlorinase from strain Viet1. Since the dehalogenases from both organisms are membrane-bound, but can be solubilized by a detergent treatment, we anticipate to complete the purification and characterization of at least one dechlorinase within the next 6 months.
(4) Localization of the reductive dechlorinases in the highly enriched cis-DCE, VC, or 1,2-D dechlorinating cultures, as well as in the PCE to ETH dechlorinating co-culture. This task will be completed within the next 4 months.

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Biofiltration of Volatile Pollutants: Engineering Mechanisms for Improved Design, Long-term Operation, Prediction and Implementation

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Research Objective

Biofiltration systems can be used for treatment of volatile organic compounds (VOCs); however, the systems are poorly understood and are currently operated as "black boxes". Common operational problems associated with biofilters include fouling, deactivation, and overgrowth, all of which make them ineffective for continuous, long-term use. The objective of this investigation is to develop generic methods for long-term stable operation, in particular by using selective limitation of supplemental nutrients while maintaining high activity. As part of this effort, we will provide deeper fundamental understanding of the important biological and transport mechanisms in biodestruction of sparingly soluble VOCs and extend this approach and mathematical models to additional systems of high priority EM relevance - direct degradation and cometabolic degradation of priority pollutants such as BTEX and chlorinated organics.

Research Progress and Implications

This report summarizes work after 2 years of a 3-year project. Major results are enumerated and discussed below.

1. Control of biofilm overgrowth, while sustaining high degradation rates, in operating trickle-bed bioreactors was accomplished by limiting selected nutrients. Optimal results were achieved by limiting either ammonium, sulfate, or calcium in the liquid recycle stream. Each of these allowed for decoupling of growth and degradation such that long-term operation was possible. Other nutrients examined, including chlorine, magnesium, phosphate, and nitrate, were not effective and resulted in either continued growth or minimal degradation rates.
2. A comprehensive two-dimensional predictive model was developed to elucidate mass transfer and kinetic limitations in these systems. This model can be extended to a variety of columnar biofiltration systems by changing appropriate parameters. This user-friendly model/program can be installed and run independently on any IBM-compatible personal computer using Microsoft Windows 95/98.
3. Fundamental measurements of Henry's law coefficients for a variety of sparingly soluble alkanes in biomass were made; results indicated that these compounds have substantially higher solubilities in aqueous biomass than in pure water. Since predictive calculations for bioprocesses are strongly affected by the magnitude of the Henry's law parameters, new correlations/measurements are needed to compensate for this effect.
4. Isolation of the VOC-degrading microorganism present in the trickle bed consortium was accomplished. Identification is pending.
5. Non-cometabolic degradation of a model chlorinated organic (1-chloropentane) was demonstrated in an operating trickle-bed system. This work is unusual because most dechlorination processes require the presence of an additional substrate before degradation of the target contaminant can be removed.
6. Three biofiltration units were assembled, inoculated with the VOC-degrading microbial consortium selected for use in this project, and have been operating continuously using selective

nutrient limitation for 1.5 years. The units are approximately one meter long with 2-inch internal diameters and constructed of glass, teflon, and stainless steel. Each unit is temperature-controlled and can be operated under a variety of continuous or recycling modes. This work represents a substantial breakthrough in filter operation by eliminating overgrowth of biomass in the column. Non-growth associated degradation kinetics have been measured and do not incur a substantial decrease in removal capacity as compared with growth-associated removal. Prolonged starvation via elimination of supplemental nutrient(s) will eventually result in decreased capacity but requires at least six months before changes are noticeable.

7. Measurements of mass transfer and kinetics were made for trickle-bed columns and indicated that kinetic limitations dominated all three systems under normal operating conditions (room temperature, moderate flow rates).
8. Quantification of biomass regeneration after prolonged starvation has been accomplished. Biofiltration units operated under nutrient-limited conditions began losing removal capacity after approximately six months. Upon reintroduction of supplemental nitrogen, in the form of ammonium, rates rose rapidly as the biomass underwent regeneration. This procedure was found to be complete in less than 14 days, after which the columns operated at 100% of their previous removal efficiency. This is the first example of quantification/qualification of biomass regeneration after prolonged starvation in a trickle-bed system.
9. Removal competence for C_2- to C_6-alkanes has been demonstrated using the microbial consortium. In addition, the consortium was able to non-cometabolically degrade 1-chloropentane. The kinetic pathway or pathways are currently unknown.

Planned Activities

Work during the following year will focus on:

1. Measurement of Henry's law coefficients measurements for sparingly soluble gases in biomass and development of correlations for the observed enhanced solubility effect
2. Extension of the mathematical model to other biofiltration systems
3. Publication of the model/Windows 95 program code on the World Wide Web
4. Measurement of fundamental kinetics and mass transfer parameters for trickle bed bioreactors for removal of BTEX and chloro-organic contaminant treatment
5. 16s-rRNA gene sequencing of the microbial isolate responsible for alkane consumption; subsequent development will allow for examination of consortial population dynamics within column reactors

Other Access To Information

A number of peer-reviewed publications have been submitted and/or accepted based on some of the results from this work. Several presentations at national scientific conferences have been given or are currently scheduled to be delivered during this calendar year. A complete list of submitted papers and presentations may be found below. Plans are underway for making these web accessible at **http://www.ornl.gov/divisions/ctd/Chem_Dev/Biochemical/biochem.htm**

Francisco, A.F., J.W. Barton, K.T. Klasson, and B.H. Davison, "Nutrient Limitation Effects on a Microbial Consortium in Trickle-Bed Bioreactors," submitted for publication.

Barton, J.W., B.H. Davison, K.T. Klasson and C.C. Gable III, "Estimation of Mass Transfer and Kinetics in Operating Trickle-bed Bioreactors for Removal of VOCs," accepted for publication in Environmental Progress.

Klasson, K.T., B.H. Davison, J.W. Barton and J.E. Jacobs, "Removal of Chlorinated and Non-chlorinated Alkanes in a Trickle-bed Reactor," accepted for publication in the proceeding of Air & Waste Management Association's 91st Annual Meeting & Exhibition.

Barton, J.W., X.S. Zhang, K.T. Klasson and B.H. Davison. Predictive Mathematical Modeling of Trickling Bed Biofilters For Elucidating Mass Transfer and Kinetic Effects," accepted for publication in the proceeding of Air & Waste Management Association's 91st Annual Meeting & Exhibition.

Barton, J.W., S.M. Hartz, K.T. Klasson and B.H. Davison, "Microbial Removal of Alkanes From Dilute Gaseous Waste Streams: Mathematical Modeling of Advanced Bioreactor Systems," accepted for publication in Journal of Chemical Technology and Biotechnology.

Barton, J.W., K.T. Klasson and B.H. Davison, "Extended Operation and Control of Biomass Overgrowth in Biofilters Designed for VOC Removal," Proceedings of the 90th Annual Meeting & Exhibition of Air and Waste Management Association, Toronto, Ontario, Canada, (1997).

Barton, J.W., K.T. Klasson, L.J. Koran Jr. and B.H. Davison, "Microbial Removal of Alkanes From Dilute Gaseous Waste Streams: Kinetics and Mass Transfer Considerations," *Biotechnology Progress*, 13, 814-821 (1997).

Microbial Mineral Transformations at the Fe(II)/Fe(III) Redox Boundary for Solid Phase Capture of Strontium and Other Metal/Radionuclide Contaminants

F. Grant Ferris, University of Toronto

Research Objective

Determine microbiological and geochemical controls on carbonate mineral preciptation reactions, and identify contributions of these processes to the solid phase capture of strontium and other metal/radionuclide contaminants. The study is relevant to the development of new clean-up strategies for DOE sites where strontium and other metal/radionuclides exist as ubiquitous and often mobile contaminants.

Research Progress and Implications

The work summarized in this report encompasses two years of a three-year project investigating the use of bacteria to concentrate and immobilize strontium, as well as other metal/radionuclide, contaminants. Major accomplishments to date include completion of metal sorption studies with bacteria and hydrous ferric oxides (HFO), assessment of the impact of strontium on bacterial Fe(III)-reduction, induction of carbonate mineral precipitation and solid phase capture of strontium under Fe(III)-reducing conditions, and discovery of a procedure to attain rapid high-level concentration of strontium in microbiologically produced calcite.

Applying principles of surface complexation theory to the strontium sorption studies has yielded equilibrium sorption constants and maximum binding capacities for HFO, and bacteria. Bacterial and HFO sorption of uranium, copper, and cadmium has also been measured. These results have revealed pronounced differences not only in the pH and time dependence of metal retention by HFO and bacteria, but also significant variations in sorption constants and sorption capacities. This information argues strongly for a paradigm shift in geochemical modeling to incorporate the influence of bacteria into studies focused on the reactive transport of metals in contaminated groundwater.

The rate and extent of bacterial Fe(III)-reduction were not negatively influenced by elevated concentrations of strontium (1.0 mM) in culture media. Similarly, strontium did not alter the pH increase that accompanies the reduction of HFO during bacterial growth. The benign impact of strontium on bacterial activity implies that toxicity is not a major concern for potential bioremediation applications. At the same time, bacterial Fe(III)-reduction contributed to substantial mineralogical transformation of substrate HFO, including formation of the Fe(II)-carbonate, siderite. When present, the solid phase partitioning of strontium was enhanced by these mineral transformation reactions. Dissolved strontium levels decreased by 10 percent over a 30 day period with solid phase distribution coefficients ranging from 10^2 to 10^3.

Elevated solid phase concentrations of strontium (up to 2.0 weight percent) were attained in less than one day by using bacterial urea hydrolysis to produce calcium carbonate (calcite) with decreases in dissolved strontium concentrations of up to 90 percent. Solid phase distribution coefficients approached four orders of magnitude (10^4). This discovery demonstrates that solid phase capture

of strontium by microbial carbonate mineral precipitation is not only feasible, but can be highly effective and accomplished in a rapid fashion.

Considerable potential exists to adapt this novel immobilization concept to the development of new clean-up strategies for DOE sites where strontium and other metal/radionuclides exist as ubiquitous and often mobile contaminants. At this early stage, further laboratory investigations and confirmation of process performance under model field conditions are considered to be the most appropriate course of action.

Planned Activities

The focus of work in the next year will be on strontium immobilization experiments in microcosms (months 20-26) and columns (months 27-36) incorporating natural and synthetic HFO-coated sands to investigate bacterial controls on the solid phase capture of metal/radionuclide contaminants under model field conditions, as outlined in the original project proposal.

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3. Leonardo, M.R., F.G. Ferris, and E.E. Roden. 1998. Analysis of iron-carbonate mineral formation during microbial reduction of synthetic amorphous iron oxide. American Society for Microbiology General Meeting, Abstract Volume, p. 379.
4. Warren, L.A., F.G. Ferris and E.E. Roden. 1997. Strontium reactions at Shewenella and hydrous ferric oxide (HFO) surfaces. Geological Society of America Annual Meeting, Abstract Volume, p. 128.
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Containment of Toxic Metals and Radionuclides in Porous and Fractured Media: Optimizing Biogeochemical Reduction versus Geochemical Oxidation

Philip M. Jardine, Oak Ridge National Laboratory

Scott C. Brooks, Oak Ridge National Laboratory

Research Objective

The purpose of this research is to provide an improved understanding and predictive capability of the mechanisms that allow metal-reducing bacteria to be effective in the bioremediation of subsurface environments contaminated with toxic metals and radionuclides. The study is motivated by the likelihood that subsurface microbial activity can effectively alter the redox state of toxic metals and radionuclides so that they are immobilized for long time periods. Our objectives are to: (1) develop an improved understanding of the rates and mechanisms of competing geochemical oxidation and microbiological reduction reactions that govern the fate and transport of redox-sensitive metals and radionuclides in the subsurface, and (2) quantify the conditions that optimize the microbial reduction of toxic metals and radionuclides, for the purpose of contaminant containment and remediation in

heterogeneous systems that have competing geochemical oxidation, sorption, and organic ligands. The overall goal of this project is to use basic research to develop a cost effective remediation strategy that employs in-situ contaminant immobilzation. Specifically, we will develop active biowall technologies to contain priority EM contaminant plumes in groundwater.

Research Progress and Implications

This report summarizes work after 1.5 y of a 3 y project.

Progress and relevance to EM needs

In an effort to control the off-site migration of redox sensitive metals (Cr) and radionuclides (Co, U, and Tc), research within this project is using metal-reducing bacteria to stabilize contaminant plumes in the subsurface. Our challenge is to optimize microbial reduction processes in the presence of competing geochemical oxidation and sorption reactions, and to sustain microbial reduction processes in-situ for long periods of time. Our approach involves the use of: (a) a sophisticated dynamic flow technique to quantify geochemical oxidation/sorption and microbial reduction rates and mechanisms controlling the mobility of U, Cr, and Co-EDTA in heterogeneous soils/sediments, (b) novel spectrophotometric techniques to monitor the time-dependent redox transformations and immobilization of U, Cr, and Co-EDTA by subsurface media, and (c) an advanced numerical model that couples hydrologic-biogeochemical transport processes for simulation of the experimental data.

To date, we are the first research group to demonstrate the sustained microbial reduction of ^{60}Co(III)EDTA to ^{60}Co(II)EDTA under dynamic flow conditions. The net reduction of the ^{60}Co(III)EDTA dominates the fate and transport of this contaminant, even in the presence of strong mineral oxidants commonly found in the subsurface (e.g., Mn- and Fe-oxides). The environmental implications of these findings are pronounced since ^{60}Co(III)EDTA is extremely stable, and this enhances its persistence and transport in subsurface environments. By discovering a way to keep the bacteria healthy and growing, we were able to effectively stabilize ^{60}Co(II)EDTA in a flowing subsurface system. This is advantageous from a remedial perspective since ^{60}Co(II)EDTA is a weaker complex than ^{60}Co(III)EDTA, and therefore easier to decouple and remediate.

The fate and transport of U(VI) and U(IV) in ORNL, Savannah River, and Hanford sediments have been quantified for a variety of environmental conditions. Investigations are emphasizing the effects of geochemical oxidation and interfacial sorption reactions, and the effects of biological reduction processes on the time-dependent mobility of U in the subsurface media. The reduction is generally quite rapid, with time scales on the order of minutes to hour. The reduction of U(VI) is advantageous from an environmental perspective since reduced U(IV) is significantly less soluble and less mobile in subsurface environments relative to the oxidized species. A unique aspect of this research is our use of time-resolved X-ray Absorption Spectroscopy (XAS) located at the Stanford Synchrotron Radiation Laboratory, in Stanford CA. Since this technique is sensitive to metal redox shifts and interfacial surface reactions, we used XAS to quantify the time-dependent bacterial reduction of U(VI) to U(IV).

The fate and transport of Cr(III) and Cr(VI) in ORNL, Savannah River, and Hanford sediments have been quantified for a variety of environmental conditions. The reduction of Cr(VI) to Cr(III) is desirable from an environmental perspective since Cr(VI) is a potent carcinogen and highly mobile in the environment, whereas Cr(III) is significantly less soluble and less toxic. Bacterial reduction of Cr(VI) to the less toxic and less mobile Cr(III) species seems improbable due to toxicity considerations. Fortunately we have discovered two alternative routes to reduce Cr(VI). The first route is abiotic, where natural organic carbon (NOM) is used to effectively reduce Cr(VI) to Cr(III) thereby slowing its subsurface mobility many orders of magnitude. This technique shows real promise for use in geochemical barriers since NOM sorbs extremely well to soils and sediments and serves as an efficient, cost effective means of immobilizing Cr. The second route uses metal reducing bacteria to reduce Fe-oxides to Fe(II), where the latter quickly reduces Cr(VI) to Cr(III). The process is catalytic where the only reactant being lost is Cr(VI). The technique shows promise for use in active biowall technologies for the in-situ containment of Cr. The efficiency of both techniques for immobilizing Cr has been quantified using time-resolved XAS since this instrument probes for

contaminants on the surface of sediments and bacteria, thereby permitting the determination of the contaminant chemical and structural state.

Planned Activities

Investigation of strategies to optimize U(VI) immobilization using metal reducing bacteria. Experiments will use realistic dynamic flow conditions to quantify microbial induced U(VI) reduction in the presence of competing geochemical sorption reactions. Completed by mid FY99.

Pursue indirect immobilization strategies for Cr(VI) in DOE soils and sediments. Experiments will focus on abiotic reduction strategies using natural organic carbon and microbial reduction strategies using reduced products of Fe-oxides to convert Cr(VI) to the highly immobile Cr(III) species. Completed by mid FY99.

Continue to use X-ray Absorption Spectroscopy at the Stanford Synchrotron Light Source to define the mechanisms of Cr(VI) and U(VI) reduction by bacteria and subsequent immobilization by soils and sediments. Completed by end of FY99.

Simulate our experimental data with the newly developed biohydrogeochemical model and use the calibrated code to assist with various DOE site needs. Completed by end of FY99.

Propose pilot scale bioreduction experiments using undisturbed cores and large scale blocks instrumented with active biowalls.

Propose field scale bioreduction demo at a Well Characterized Field Tracer Facility on the Oak Ridge Reservation (see **http://www.esd.ornl/facilities/hydrology/WAG5/).**

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Advanced Experimental Analysis of Controls on Microbial Fe(III) Oxide Reduction

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Matilde M. Urrutia, University of Alabama

Research Objective

Understanding factors which control the long-term survival and activity of Fe(III)-reducing bacteria (FeRB) in subsurface sedimentary environments is important for predicting their ability to serve as agents for bioremediation of organic and inorganic contaminants. This project seeks to refine our quantitative understanding of microbiological and geochemical controls on bacterial Fe(III) oxide reduction and growth of FeRB, using laboratory reactor systems which mimic to varying degrees the physical and chemical conditions of subsurface sedimentary environments. Methods for studying microbial Fe(III) oxide reduction and FeRB growth in experimental systems which incorporate advective aqueous phase flux are being developed for this purpose. These methodologies, together with an accumulating database on the kinetics of Fe(III) reduction and bacterial growth with various synthetic and natural Fe(III) oxide minerals, will be applicable to experimental and modeling studies of subsurface contaminant transformations directly coupled to or influenced by bacterial Fe(III) oxide reduction and FeRB activity.

Research Progress and Implications

This report summarizes research accomplished after approximately 1.5 yr of a 3-yr project. A central hypothesis of the research is that advective elimination of the primary end-product of Fe(III) oxide reduction, Fe(II), will enhance the rate and extent of microbial Fe(III) oxide reduction in open experimental systems. This hypothesis is based on previous studies in our laboratory which demonstrated that association of evolved Fe(II) with oxide and FeRB cell surfaces (via adsorption or surface precipitation) is a primary cause for cessation of Fe(III) oxide reduction activity in batch culture experiments. Semicontinuous culturing was adopted as a first approach to test this basic hypothesis. Synthetic goethite or natural Fe(III) oxide-rich subsoils were used as Fe(III) sources, with the Fe(III)-reducing bacterium Shewanella alga as the test organism.

Average residence times of 90, 18, 9, or 4.5 d were established by replacing 1, 5, 10 or 20 mL of the aqueous phase of the cultures (30 mL total volume) with fresh sterile, anaerobic culture medium every 3 d. Consistent with our basic hypothesis, replacement of 5-20 mL of medium (4.5-18 d residence time) resulted in a 2-4 fold increase in the cumulative amount of Fe(II) produced in the cultures over a 2 month incubation period, relative to that occurring in parallel batch cultures. Fe(III) reduction in the semicontinuous cultures showed little or no sign of slow-down at the end of the experiment, whereas reduction had virtually ceased in the batch cultures. A two-fold increase in the extent of synthetic goethite reduction was also observed in an experiment conducted with a continuous-flow stirred reactor (CFSTR) with a residence time of 2-3 d.

In all cases the enhanced reduction was accounted for by generation of dissolved Fe(II) which was periodically removed from the cultures during aqueous phase replacement. The Fe(II) content of the solid-phase (sorbed or precipitated) was lower in the semicontinuous and CFSTR systems, which suggested that aqueous phase flux led to significant Fe(II) desorption or reduced solid-phase association. Together these results indicate that the primary basis for the stimulation of Fe(III) oxide reduction was removal of the major end-product of oxide reduction, i.e. Fe(II). Our findings demonstrate that aqueous phase transport and attendant elimination of reaction end-products could play an important role in governing the in-situ rate and persistence of microbial Fe(III) oxide reduction activity in anaerobic subsurface sediments. This in turn may have an important impact on the survival

and activity of FeRB to be exploited for bioremediation purposes (e.g. the reductive immobilization of uranium, chromium, cobalt, and other metal/radionuclide contaminants; oxidation of hydrocarbon contaminants; reductive dechlorination of chlorinated solvents). An important implication of these findings is that models describing bacterial Fe(III) oxide reduction in subsurface environments will have to account for the fate of evolved Fe(II), and relate this in some manner to the abundance of available Fe(III) reduction sites and the viability of Fe(III)-reducing bacteria.

Other significant research accomplishments generated by this project include: (1) a detailed analysis of the growth rate and biomass yield (derived from measurements of cell protein production) of two representative FeRB (S. alga and Geobacter metallireducens) growing with different forms of synthetic Fe(III) (ferric citrate, amorphous Fe(OH)3, a-FeOOH) as an electron acceptor. Results indicate that despite considerable differences in the rate and pattern of Fe(III) reduction and FeRB growth, an approximately consistent long-term biomass yield of 5 to 15 mg protein per mmol Fe(III) reduced was observed with the different forms of Fe(III). These results provide a useful point of departure for quantitative modeling of FeRB growth and metabolism in various types of experimental and in-situ anaerobic sedimentary systems; (2) a preliminary examination of the use of ^{3}H-leucine incorporation for measuring short-term (essentially instantaneous) FeRB (G. metallireducens and S. alga) growth rates during reduction of soluble and solid-phase Fe(III). Results suggest that G. metallireducens, unlike S. alga, lacks the ability to express a high rate of exogenous leucine incorporation (probably due to the lack of an "active" cell membrane leucine uptake system). An important implication of this finding is that ^{3}H-leucine incorporation may not be an appropriate means of estimating FeRB growth rates in natural sediments in which Geobacter dominates Fe(III) reduction activity.

Another important implication of this study is that rates of S. alga biomass production estimated from 3H-leucine incorporation with 10-1000 nM total leucine concentration were much lower than those inferred from independent measurements of biomass yield during Fe(III) reduction, probably because of isotope dilution by de novo leucine biosynthesis. A subsequent experiment indicated that additions of at least 1 mM total leucine are required to repress de novo biosynthesis during short-term (0.5-2 hr) ^{3}H-leucine incorporation experiments in culture medium. Rates of protein production during growth of S. alga on ferric citrate estimated from ^{3}H-leucine incorporation with 1 mM total leucine agreed within a factor of 2 with independent estimates of bacterial protein production. This result indicates that ^{3}H-leucine incorporation can provide a quantitatively valid method for tracking instantaneous bacterial growth rates in experimental Fe(III) reduction systems.

Planned Activities

Manuscripts on the initial semicontinuous culture work and the FeRB growth/biomass production study are in preparation and will be submitted for publication by September 1998. A detailed series of experiments using the semicontinuous culture systems is in progress, examining the influence of various aqueous phase components (chelators, dissolved inorganic carbon, humic substances) on the rate and extent of natural and synthetic Fe(III) oxide reduction; this work will form the basis of a manuscript to be submitted for publication early next year. Completion of two papers dealing with ^{3}H-leucine incorporation by FeRB and the use of ^{3}H-leucine incorporation to measure FeRB growth rates is anticipated by the end of the year. A broad-ranging study of the rate/extent of natural and synthetic Fe(III) oxide reduction and associated FeRB growth will be initiated this summer to examine how the mineralogy and Fe(III) oxide abundance of natural soils and sediments may quantitatively control the growth and metabolism of these organisms; this study will combine measurements of gross biomass production with ^{3}H-leucine based estimates of instantaneous FeRB growth rates during the active growth phase of batch culture systems. Initiation of experiments on Fe(III) oxide reduction and FeRB growth in CFSTR and column reactor systems will occur early this Summer; the main thrust of research activity on this project will become focused on these experimental systems starting in the Fall of 1998.

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Stable Isotopic Investigations of in-situ Bioremediation of Chlorinated Organic Solvents

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Research Objective

Contamination of soils and groundwaters with chlorinated aliphatic hydrocarbons (CAHs) is one of the most serious environmental problems in the DOE system and in the nation at large. These compounds are designated as priority pollutants by the U.S. Environmental Protection Agency (EPA) and are known or suspected to be carcinogenic or mutagenic in humans. These compounds are readily transported by groundwater and are not reduced to acceptable concentrations for human consumption by most municipal water supply treatments; thus the compounds represent a significant hazard to a large portion of the human population. In situ bioremediation is an emerging technology that shows great promise for mitigation of CAH contamination at many sites.

One of the most severe limitations of in-situ bioremediation is the difficulty of proving when it is working at a given site. The concentrations of CAHs and their degradation products in plumes may be difficult to relate to the efficiency of the remediation process because of dilution effects, but this problem is mitigated to a large extent by measuring isotope ratios. If there is a significant isotopic fractionation between CAHs and derivative chlorine-bearing products, then the fraction of CAH that is dechlorinated can be inferred from the $^{37}Cl/^{35}Cl$ and $^{13}C/^{12}C$ isotope ratios of the residual CAH. It is important to point out that there is currently no published information available on the magnitude of chlorine and carbon isotopic fractionation associated with biological degradation of CAHs. We plan to help eliminate this important gap in our knowledge with the work being performed here.

This work is relevant to EMSP goals because it will provide a new and cost-effective means of evaluating and monitoring the effectiveness of in-situ bioremediation. It will employ newly developed techniques to characterize isotopic fractionation (of chlorine and carbon) associated with biotic and abiotic degradation of CAHs in laboratory microcosms. These techniques and the data acquired by using them in laboratory studies will form the fundamental basis for quantitative assessment of the mechanisms, rates, and efficiencies of various in-situ bioremediation schemes for CAHs.

Research Progress and Implications

This report summarizes work as of 21 months into a 36-month project. First, we have developed methods for precise measurement of stable carbon and chlorine isotope ratios of micromolar amounts

of CAHs. We have also developed methods for quantitative extraction of CAHs from water and air. We have applied these methods in laboratory experiments, to investigate isotopic fractionation caused by microbial degradation and by abiotic processes such as evaporation and chemical reduction. We have also applied these methods to field investigations of contaminated groundwater aquifers at the Paducah Gaseous Diffusion Plant, Kentucky and at several manufacturing plants in the Chicago and Kansas City metropolitan areas. Results of much of this work have already been incorporated into four manuscripts that have been published, accepted for publication, or are in review (see references below).

The microbial degradation of CAHs can cause large isotopic fractionation of carbon and chlorine isotopes. The carbon isotopic fractionation is about 11 times as large as the chlorine isotopic fractionation in the system that we have best characterized to date (aerobic degradation of dichloromethane [DCM]). The carbon isotopic fractionation during aerobic microbial degradation of DCM (42.4 per mil) is about twice as large as that during microbial oxidation of methane, and the chlorine isotopic fractionation is about 3.8 per mil (Heraty et al., 1998), with the residual DCM being enriched in the heavy isotopes. Our preliminary results show that the isotopic fractionation between CAH liquids and vapors is much smaller than that caused by microbial degradation. The carbon isotopic fractionation between CAH liquids and vapors is such that the vapor is enriched in the heavy isotope, so the residue of evaporation is isotopically depleted in the heavy isotope. This finding allows the isotope effects of microbial degradation to be readily distinguished from those of evaporation, and thus is immediately applicable in the field.

Planned Activities

During the remaining time of this program, we will proceed further with all three of our primary tasks: analytical and sampling methods development, laboratory experiments, and field studies. In the analytical and sampling methods development task, we plan to implement a continuous-flow capability for on-line Cl isotope ratio measurement of very small (i.e., <0.1 micromole) samples of CH_3Cl on our mass spectrometer. The ability to analyze such small samples is necessary for field studies of contaminated aquifers, where concentrations of chlorinated VOCs may be only in the ppb range. This will lead to the eventual ability to perform compound-specific Cl isotope analysis of mixtures of chlorinated VOCs. In the laboratory experiment task, we will continue our ongoing series of liquid culture and soil column experiments with aerobic and anaerobic microbes. We will also continue our investigation of abiotic processes that may fractionate stable isotopes, such as evaporation and adsorption, as well as the potential of Fe-bearing minerals for abiotic degradation of chlorinated VOCs. In the field studies task, we plan to study CAH plumes at several more well characterized sites.

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Reduction and Immobilization of Radionuclides and Toxic Metal Ions Using Combined Zero Valent Iron and Anaerobic Bacteria

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Research Objective

Previous research findings indicate that both zero valent iron and sulfate reducing bacteria (SRB) can yield significant decreases in Cr(VI) or U(VI) concentrations due to abiotic and microbial reduction, respectively. The major hypothesis associated with this research project is that a combined abiotic-biological system can synergistically combine both processes to maximize metal ion reduction in an engineered permeable reactive barrier. The overall goal of this project is to design a combined abiotic/microbial, reactive, permeable, in-situ barrier with sufficient reductive potential to prevent downgradient migration of toxic metal ions. The field-scale application of this technology would utilize anaerobic digester sludge, Fe(0) particles for supporting anaerobic biofilms, and suitable aquifer material for construction of the barrier. Successful completion of this goal requires testing of the two hypotheses listed above by evaluating: (1) the rates of abiotic metal ion reduction, and (2) the rates of microbial metal ion reduction in microbial and combined abiotic/microbial reduction systems under a range of environmental conditions.

Research Progress and Implications

This report summarizes work after one and one-half years of a three year project.

Abiotic studies: The thrust of the abiotic research conducted to date has been to determine the rates of Cr(VI) reduction in batch reactors and to evaluate the role of aquifer materials on those rates. Experiments have been conducted to determine the rates of reduction by Fe(II) and Fe(0). The parameters that have been evaluated are the effect of pH and the presence of sulfide and aquifer material.

All reactions were conducted in a 1.5-L jacketed reaction vessel. Degassed water was used in all experiments and was prepared by bubbling 99.999% Ar through boiled Nanopure water. Dissolved oxygen levels could be reduced to below 5 ppb in this manner. The experiments were conducted in a glove bag under Ar. The water jacket was used to maintain a temperature of 23° C. The mixing rate was maintained at 400 rpm.

It has been proposed that the diphenylcarbazide (DPC) spectrophotometric method for measuring Cr(VI) could lead to incorrect measurements in the presence of Fe(II) (1). At the low pH of the DPC reagent, the Fe(II) reaction with Cr(VI) is extremely rapid and may continue simultaneously causing errors in the Cr(VI) measured. A spectral-fitting method has been used to measure Cr(VI) without the addition of any colorimetric reagents (1). In this method the molar extinction coefficients of CrO_4^{2-}, $HCrO_4^{1-}$, Fe^{3+}, $Fe(OH)^{2+}$ and $Fe(OH)_2^{1+}$ are determined over a range of wavelengths. This spectral data is then manipulated in order to solve for the Cr(VI) concentration when the absorbance spectra of a sample are measured. In our research, both the spectral fitting method and the DPC method were examined. Both methods yielded reproducible results under the conditions examined. In addition, experiments conducted to examine the reduction of Cr(VI) by Fe(II) using the DPC method yielded rate constants that were similar to those reported by Buerge and Hug (1).

Preliminary experiments investigating the reduction of Cr(VI) by Fe(II) have been conducted for the purpose of establishing the kinetics in our system over a range of pH. The kinetic data fits the second-order rate law proposed by Buerge and Hug (1).

Experiments have been conducted to evaluate the reduction of Cr(VI) by zero-valent iron (Fe(0)). The reaction of Cr(VI) with Fe(0) alone was examined over a range from pH=5.5 to pH=7. In each case 20 grams of commercial grade iron filings were used in 1500 ml of buffered degassed water

and allowed to equilibrate for 1 hour prior to Cr(VI) addition. After this hour, high initial Fe(II) concentrations were measured. However, shortly after Cr(VI) addition, Fe(II) was rapidly depleted to below detection limits. To initiate the experiments Cr(VI) was added to yield an initial Cr(VI) concentration of 500 uM. In each experimental run an initial rapid decrease in Cr(VI) was observed followed by a region of much slower reduction. The rapid initial Cr(VI) reduction is presumably due to sorption and the presence of Fe(II) in solution. Addition of excess Fe(II) to the system led to a concomitant increase in the initial reduction of Cr(VI). As pH increases the initial drop in Cr(VI) concentration also decreases.

Chromate reduction was also evaluated for Fe(0) in the presence of other constituents (at pH=7). These include sulfide, Fe(II) and aquifer material. As in the case of Fe(0) alone, a rapid initial decrease in Cr(VI) concentration was observed followed by a region of much slower loss. The rapid initial decrease in Cr(VI) concentration was greater for those systems containing either excess Fe(II) or sulfide compared to systems containing F(0) alone or those with Fe(0) or the aquifer material tested to date. After the initial drop in Cr(VI) concentration the rate of Cr(VI) loss was similar for all systems tested containing Fe(0). The reduction of Cr (VI) was decreased by the addition of Ottawa sand which is in contrast to the enhanced reduction measured in the presence of aluminosilicates (2).

Combined abiotic-biological studies: Studies using continuous flow columns are being conducted to investigate the effect of SRB and zero valent iron on the reduction of Cr(VI). Four columns, each with a total volume of 72 mL, were constructed. Columns A, B, and C were packed with fine steel wool (5 gm), producing a porosity of 98.6%. Columns B and C were inoculated with mixed liquor from a chemostat enriched for SRB. Lactate was also added to column C influent. Column CL served as an unpacked and unseeded control. Each column was feed 10 mL/day of basal media spiked with Cr(VI) and sulfate.

The columns were first spiked with 192 μM (10 ppm) of Cr(VI). After 1.5 pore volumes the Cr(VI) concentration was increased to 384 μM (20 ppm). At these concentrations, the effluent concentrations of total chromium have been near non-detectable for each of the columns A, B and C. The pH in the effluent during both experiments ranged between 8 and 9, possibly as a result of iron corrosion.

Sulfate loss was greatest in column C, possibly due to lactate consumption. An electron balance indicates the loss of sulfate and lactate in column C is not stoichiometric.

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Planned Activities

Studies will be conducted in then next 1-1/2 years to examine and quantify Cr(VI) reduction by amorphous iron sulfide alone and in the presence of Fe(0). Also the effect of competing adsorbates and various aquifer materials on Cr(VI) reduction will be evaluated. Additional combined abiotic-biological column experiments will be conducted to examine Cr(VI) reduction at higher Cr(VI) concentrations and to quantify the stoichiometry between sulfate reduction and electron donor oxidation in the presence of elevated levels of Cr(VI).

Rapid Mass Spectrometric DNA Diagnostics for Assessing Microbial Community Activity During Bioremediation

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Research Objective

Biological activity has often been attributed to changes in pollutant profiles found in contaminated soils when abiotic processes actually caused pollutant removal. Careful evaluation of bioremediation necessitates that all transformation and removal pathways are anticipated so that the pathways are controlled or monitored. Our work is directed at evaluating a monitoring strategy that relies on the combined use of DNA diagnostic procedures and mass spectrometry as the detection scheme. The intent is to track bioremediation by measuring the occurrence of genes in soil samples that are known to code for enzymes capable of degrading specific pollutants. Matrix-assisted-laser-desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) offers the possibility for automation and high throughput PNA detection as is needed to track the course of bioremediation over large polluted areas.

Research Progress and Implications

As of last year, the first year in a three year project, we identified and sequenced a unique 161-bp region useful for identifying the nahH gene. In this second year of the project, two approaches were used to probe DNA samples for the presence of this napthalene degrading gene. The first was a Ligase Chain Reaction (LCR). In a reaction where the DNA target template is present, LCR reaction conditions were established to detect a 40-bp section of the gene by ligating two 20-bp oligonucleotide probes designed to anneal abuttingly to this target. The detection of a 40-mer oligonucleotide serves to score the test positive. In the absence of the specific target sequence, ligation should not occur and the test is scored negative. The products of the ligation reactions were analyzed by an assay incorporating alkaline phosphatase onto one of the oligonucleotides. The LCR approach is very sensitive, correctly identifying the presence of nahH using sub-attomole quantities of templat

The second approach we examined involved the use of Peptide Nucleic Acid (PNA) probes to identify a Polymerase Chain Reaction (PCR) amplicon from nahH. In this assay, double-stranded PCR products are affinity-captured to streptavidin-coated magnetic beads by means of a biotin label on one of the PCR primers. The non-biotinylated strand of DNA is denatured and removed in a wash step, after which a PNA oligomer is allowed to anneal to the captured strand. Excess PNA is then washed away while affinity-captured PNA is transferred to a MALDI-TOF-MS sample holder. The PNA is released from the complex when matrix is added. The test is scored positive when a peak corresponding to the mass of PNA^+ appears in the mass spectrum.

We observed that the PNA assay offers several advantages over the LCR approach and other existing analytical techniques for identifying the presence of genes in environmental DNA samples. PCR reactions are much less susceptible to changes in reagent concentrations than are LCR reactions, leading to higher confidence in procedures based on PCR. PNA-DNA complexes tend to be more stable than corresponding DNA-DNA complexes and therefore hybridization is easier to control. Single-base mismatches disrupt PNA-DNA stability far more than they do DNA-DNA stability, which increases the diagnostic value of the procedure.

We investigated the use of a PNA probe and MALDI-TOF-MS as a way to detect the naphthalene-degrading di-oxygenase gene in environmental soil samples. We then studied the reliability of this test by varying reaction conditions. DNA extracted from a bacterial colony known to contain naphthalene-degrading genes was amplified by PCR and allowed to hybridize with a 14-mer PNA probe. The bead-DNA-PNA complex was washed several times and added to a sinapinic acid (SA) solution. SA is used in this procedure as the MALDI matrix. The mixture was transferred to a

MALDI probe and evaporated under nitrogen. 100 fmol of pure 14-mer PNA is the lower practical limit of detection for PNA in SA measured with our MALDI-TOF mass spectrometer. The intensity of the PNA^+ signal generated with standards increased linearly with [PNA].

When bead-DNA-PNA complex was mixed with SA, PNA was not released efficiently from the target DNA unless 0.1% TFA was present. In the presence of TFA, the resulting bead-DNA, PNA and matrix solution could be evaporated to form a crystallized MALDI sample. Examination of the crystals under the microscope revealed many of the beads were incorporated into the crystals and sometimes interfered with the formation of crystals. The presence of the beads reduced the limit of detection to about 500 fmole of PNA. A plot of PNA^+ signal intensity vs. the concentration of PCR product, for a fixed concentration of the PNA probe, rises linearly. We also found that it was important to carefully optimize the conditions for denaturing the double-stranded PCR product after it was affinity captured. Even though it has been reported that Na^+ attaches less tenaciously to PNA than DNA, we frequently observed PNA mass spectra with 1 to 4 sodium ions attached to a 14-mer PNA. For this reason we attempted to denature the PCR product with 100% NH_4OH but found it to be inefficient.

Planned Activities

The MALDI technique we developed could be used to analyze a large number of samples rapidly. We are evaluating MALDI hardware modifications for conducting the analyses under computer control, thus providing a high throughput capability needed to track the course of bioremediation. The technique is easily adaptable for use in many different types of studies because it is possible to redesign the PCR primers and the PNA probe for the purpose of detecting a large number of different genes as needed to monitor the degradation of several pollutants. We will attempt to measure the occurrence of the di-oxygenase gene in environmental samples contaminated with naphthalene.

Monitoring Genetic & Metabolic Potential for In Situ Bioremediation: Mass Spectrometry

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Research Objective

A number of DOE sites are contaminated with dense non-aqueous phase liquids (DNAPLs) such as carbon tetrachloride and trichloroethylene. At many of these sites, microbial bioremediation is an attractive strategy for cleanup, since it has the potential to degrade DNAPLs in-situ. A rapid screening method to determine the broad range potential of a site's microbial population for contaminant degradation would greatly facilitate assessment for in-situ bioremediation, as well as for monitoring ongoing bioremediation treatment. Current laboratory-based treatability methods are cumbersome and expensive. In this project, we are developing methods based on matrix-assisted laser desorption/ionization mass-spectrometry (MALDI-MS) to rapidly and accurately detect polymerase chain

reaction (PCR) products. In parallel, PCR primers to amplify DNA sequences from microbial genes involved in biodegradation of pollutants are being identified that are short enough to allow MALDI-MS detection. This work will lay the foundation for development of a field-portable MS-based technique for rapid assessment and monitoring of bioremediation processes on site.

Research Progress and Implications

This report summarizes work after 1-1/2 years of a 3-year project. In this time, we have demonstrated MALDI-MS-based detection of signature bacterial PCR products (Hurst *et al.*, 1998). A model system for interfacing MALDI-MS with PCR amplification is based on the *pmoA* gene for the active site subunit of particulate methane monooxygenase, a bacterial enzyme that can oxidize trichloroethylene. PCR primer pairs were designed to amplify relatively short segments (99 bases and 56 bases) of this gene in Type I and Type II methanotrophs. A rapid reverse-phase purification of the resulting PCR products allows MALDI-MS detection from a fraction of one 25-microliter PCR reaction. At this level of sensitivity, MALDI-MS has considerable potential to compete with existing electrophoresis and hybridization methods for detecting PCR products in this size range. To allow increased throughput, the PerSeptive Biosystems MALDI-TOF mass spectrometer allows automated MALDI data acquisition, and we have adapted our purification scheme to a 96-well microtiter plate format that allows parallel treatment of 96 PCR reactions in about ten minutes (Weaver *et al.*, 1998). An in-house-constructed TOF mass spectrometer is being modified to allow more fundamental studies aimed at improving the MS detection of PCR products.

Planned Activities

In FY98/99, we will investigate effects of interferences and estimate lower limits of detection for methanotrophs using MALDI-detected PCR, and compare MALDI-detection of PCR products with accepted methods for detecting methanotrophs in environmental samples. In FY99, we will continue to explore MALDI detection for multiplexed hybridization detection of methanotroph PCR products, evaluate electron-capture ionization as a means for improving MALDI sensitivity, and pursue more reproducible and convenient methods for combining PCR products with the MALDI matrix.

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Use of Sonication for In-Well Softening of Semivolatile Organic Compounds

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Research Objective

This project investigates the in-situ degradation of semivolatile organic compounds (SVOCs) and volatile organic compounds (VOCs) using in-well sonication, in-well vapor stripping, and biodegradation. The project has the primary objectives of developing this integrated system for efficient and economical removal and degradation of SVOCs and VOCs from groundwater. The project has as its goal the partial degradation (softening) of the more recalcitrant organic compounds in order to convert them into compounds that are more amenable to both air sparging and biological treatment. By performing the softening in-well, the treated organics can be reinjected and percolated through the subsurface, thereby enhancing biodegradation by generating organics that are more easily biodegraded.

Research Progress and Implications

This report summarizes work after nearly 2 years of a 3-year project. Argonne National Laboratory is developing a new technology that combines in-well sonication, in-well vapor stripping, and in-situ biodegradation for removal of SVOCs and VOCs from solution. Bench-scale batch experiments have been performed investigating the separate treatment systems involving stripping and sonication of halogenated organics in groundwater, along with the combined sonication/stripping system. Organic contaminants studied include: trichloroethylene (TCE), carbon tetrachloride (CCl_4), tetrachloroethylene (PCE), trichloroethane (TCA), and ethylene dibromide (EDB). Initial organic concentrations range from ~10 to ~100 mg/L. Results of the sonication and vapor stripping experiments are available upon request.

For the in-well vapor stripping experiments, air flow rates of 500, 1000, and 1500 mL/min were used. Over the entire concentration range, the first order rate constant was typically in the range of 0.15 to 0.28 min(-1) for removal of CCl_4, TCE, PCE, and TCA from solution at 500 mL/min air flow rate, and 0.45 to 0.62 min(-1) for these same compounds at 1500 mL/min air flow rate. EDB was much less volatile, with rate constants ranging from 0.025 to 0.028 min(-1) and 0.056 to 0.066 min(-1) at 500 and 1500 mL/min air flow rates, respectively.

The first order rate constants obtained for CCl_4 and TCE using only sonication indicated that CCl_4 is easier to degrade than TCE. The higher the power intensity, the higher the rate constant. The rate constants also exhibit a slight concentration effect; the lower the initial chlorinated organic concentration, the higher the rate constant (albeit a slight increase). Greater differences between the degradation rates of CCl_4 and TCE are observed at the higher concentrations and higher power intensities tested. The major degradation mechanism of volatile organic compounds under ultrasonic irradiation is considered to be direct pyrolysis within the cavitation bubbles.

In an effort to describe the acoustic cavitation effects, a mathematical model has been developed that incorporates acoustic pressure produced in solution by sonication; nuclei generation contributed by gas pockets in suspended particles or pre-existing small bubbles; the onset, growth, and collapse of bubbles; and pyrolysis reactions due to the high temperature of the collapsing bubbles. Two different pathways, stable cavitation and transient cavitation, contribute to the sonochemical reactions because both processes produce high temperature and pressures to decompose organic chemicals in solution.

To analyze the halogenated compounds in solution, the methodology for gas chromatography using head space analysis has been successfully employed. Maximum sample holding times for CCl_4, TCE, and PCE, were in the order of CCl_4 > TCE > PCE. In the laboratory setting where rapid analysis of samples is possible, limited holding times were acceptable to increase the precision of the analytical results. Experiments conducted in which TCE and CCl_4 were injected together, the loss of TCE through the septum was unaffected by the presence of CCl_4 whereas the loss of CCl_4 was affected by the presence of TCE, indicating that CCl_4 loss through the septum was facilitated by the presence of TCE.

Stanford University has performed numerical modeling of the combined sonication/vapor stripping laboratory system on the basis of hypothetical parameter values. In this initial modeling effort, the contaminant of concern was assumed to be TCE. The hydraulic conductivity, porosity, and retardation factors selected are typical for a clean sand aquifer. The treatment well was placed at the center of the tank, and water was withdrawn near the bottom of the well. Two different flow rates were used to perform the simulations. For the purposes of the simulations, the sonication rate was assumed to be independent of concentration. The modeling indicates that the contaminant is removed quite rapidly, although higher concentration regions persist in the corners of the tank. Concentrations drop more rapidly at the higher pumping rate. Further modeling will indicate if there are monitoring locations at which the effects of sonication are more pronounced. The effect of sonication is likely to have the greatest effect for relatively nonvolatile compounds such as EDB.

Preliminary efforts at the California Institute of Technology (CIT) have determined that the optimum ultrasonic frequency for the degradation of CCl_4 is around 500 kHz. The CIT work has also identified the degradation products following the sonication of CCl_4, $CHCl_3$, and CH_2Cl_2. The intermediate degradation products identified include: C_2Cl_4, C_2Cl_6, CCl_4, and $CHCl_3$. CIT has initiated some preliminary modeling efforts for the various mechanisms of the sonication/degradation of the VOCs and SVOCs.

Planned Activities

Bench-scale research experiments will continue to be performed involving sonication and vapor stripping of the various halogenated organic compounds. Batch sonication and air stripping experiments will be completed by the end of FY 1998, moving towards the continuous flow treatment. Methods to enhance the reaction rate constants will be examined (e.g., application of higher ultrasonic frequencies; addition of oxidants such as ozone, hydrogen peroxide, etc.). Preliminary optimal conditions will be identified for the operation of the continuous flow system. The corrosion potential and salt formation potential will be identified and quantified. Chemical reaction mechanisms will be modeled. A 3-D computer model simulation is being developed to describe the combined sonication/vapor stripping/biodegradation system for simulating field operation. During FY 1999, a large laboratory-scale pilot system will be tested for application prior to field demonstration.

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Electrochemical Processes for In-Situ Treatment of Contaminated Soils

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Research Objective

This research project is to develop electrochemical processes for in-situ treatment of contaminated soils. Specifically, it is to study electrokinetic (EK) and electro-Fento (EF) processes and to integrate these processes for the treatment of soils containing mixed contaminants. Our objectives are:

- To study important parameters controlling the mobilization and the transport of selected organics and metals in soils by the electrokinetic (EK) process. Factors to be studied include field strength, pH, ionic strength, soil washing agents, types of organic and metal contaminants, and soil surface properties such as cation exchange capacity(CEC), soil organic content, soil moisture content, soil composition, and surface charge.
- To study the important factors governing the oxidation of selected organic contaminants by the electro-Fenton (EF) process. Parameters such as pH, surface area and the configuration of working electrode, oxygen concentration, ferrous ion, and temperature that may affect the performance of the EF process will be investigated.
- To understand the mechanism of the oxidation of selected organic contaminants by the electro-Fenton oxidation process.

Research Progress and Implications

As of June 1998, this research project was in the midterm of the second year of a three-year project. During the last 18 months, we have completed the following laboratory studies:

- Physical Chemical Characterization of Soil Samples

  The characterization of the physical chemical properties of six soil samples. These soil samples were obtained from the Argonne National Laboratory and were collected from an undisclosed DOE site. These soil samples were characterized thoroughly for composition, soil pH, soil organic content, soil moisture content, soil cation exchange capacity, specific surface area, pH_{zpc}, hydraulic conductivity, organic contaminants, and heavy metals.

- Adsorption of Selected Organic Compounds onto Soils

  In order to understand the nature of the association of organic chemicals with soil, laboratory experimenrs were conducted to evaluate the adsorption characteristics of the selected organic chemicals onto soil samples. The following organic chemicals were evaluated: chlorophenols (4-chorophenol, 2,4-dichlorophenol, and 2,4,5,-trichlorophenol) trichloroethylene (TCE), tetrachloroethylene (PCE) and naphthalene. The major factor studied was the soil-solution ratio and the effect of a co-solvent. Results indicate that the uptake of organic compounds by soils is affected by the soil solution ratio. Generally, the amount of organic adsorbed per unit mass of the soil sample increases with decreasing soil concentration. Results also indicate that the presence of a co-solvent such as methanol will decrease the uptake of organic chemicals by soils.

- Removal of Selected Organic Compounds from Soils by Electrokinetic Process

  Both enhanced and unenhanced electrokinetic experiments were conducted. In the unenhanced mode, no pH control was attempted; pore water was electrolyzed to produce proton and

hydroxide ions. The pH profile of the soil column changes. In the enhanced mode, the pH of the cathodic chamber and the anodic chamber were controlled. Results indicate that controlled or enhanced electrokinetic processes are advantageous compared to the unenhanced mode. A neutral pH condition can achieve high energy efficiency and organic removal. This is accomplished by the use of sodium acetate and acetic acid, instead of a strong acid and a strong base, as pH modifiers. Results indicate that electrokinetic process can effectively remove organic contaminants such as chlorophenols (phenol, 2-chloro phenol, 3-chloro phenol, 4-chloro phenol and 2,3,5 tri-chlorophenol). As high as 90% organic removal can be achieved in 15 days.

- Electrochemical Generation of Hydrogen Peroxide

  Laboratory experiments were conducted to generate hydrogen peroxide using the electrochemical method. The generation of hydrogen peroxide as affected by current density, temperature, oxygen supply, pH and cathode configuration were evaluated. Results indicate that under a current density of 1 mA/cm^2, a pH of 3, and a temperature of 25 ^oC, the amount of hydrogen peroxide generation will be optimal. Pure oxygen and small oxygen bubbles are also crucial to the generation of hydrogen peroxide. Increasing surface area will increase the output of hydrogen peroxide. As high as 200 ppm hydrogen peroxide can be generated under the following conditions: 100% oxygen at a flow rate of 2000 cm^3/min, 25 ^oC, 0.05 M ionic strength, 1 Amp, 754 cm^2 cathode.

- Oxidation of Selected Organic Compounds by Fenton's Reagent

  Laboratory experiments were conducted to evaluate the efficiency of the mineralization of selected organic compounds, TCE, PCE, Naphthalene, and chloroform. Results indicate that Fenton oxidation process is very effective in mineralizing these organic compounds (except chloroform due to the degree of saturation in C-H bounding) Oxidation reactions proceed rapidly to completion. For example, in 2 minutes for the oxidation of TCE with 10^{-2} M hydrogen peroxide and $1x10^{-3}$ M ferrous ion is completed. In one minute, the oxidation of naphthalene is completed in the presence of $2x10^{-2}$ M hydrogen peroxide, $1x10^{-3}$ M ferrous ion, pH 3 and an organic concentration of 50 ppm.

- Implications

  Results obtained so far clearly indicate that an integrated electrokinetic electro-Fenton process is highly promising as an in-situ soil decontamination technique. This technology can be easily implemented.

Planned Activities

During the next half term of this research project, research activities will concentrate on the following experiments:

- *Modification of the hydrogen peroxide generation reactor*. An attempt will be made to increase the current efficiency of the electro-Fenton reactor. This is done by re-configuring the cathode. Specifically, the use of a fluidized dipolar cathode will be attempted.
- *Removal of heavy metals from soils by electrokinetic process*. Experiments will be conducted to remove heavy meals such as Cu(II), Pb(II), As(V), Hg(II), Cr(VI), and Zn(II) from soils by electrokinetic process.
- *Identify the reaction pathways of the Fenton oxidation of selected organic compounds*. Reaction pathways for the oxidation of PAHs and chlorinated organic compounds will be identified.
- *Integrate the electrokinetic and electro-Fenton oxidation processes.* Laboratory bench top EKEF reactors will be constructed to evaluate the total soil decontamination process.

Other Access To Information

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A Broad Spectrum Catalytic System for Removal of Toxic Organics from Water By Deep Oxidation

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Research Objective

Toxic organics and polymers pose a serious threat to the environment, especially when they are present in aquatic systems. The objective of the research is the design of practical procedures for the removal and/or recycling of such pollutants by oxidation.

Research Progress and Implications

This report summarizes the work performed in the first one and half years of a three year project.

We had earlier described a catalytic system for the deep oxidation of toxic organics, such as benzene, phenol and substituted phenols, aliphatic and aromatic halogenated compounds, organophosphorus, and organosulfur compounds [1]. In this system, metallic palladium was found to catalyze the oxidation of the substrate by dioxygen in aqueous medium at 80-100° C in the presence of carbon monoxide. For all the substrates examined, deep oxidation to carbon monoxide, carbon dioxide, and water occurred in high yields, resulting in up to several hundred turnovers over a 24 h period.

Because of a pressing need for new procedures for the destruction of chemical warfare agents, we have examined in detail the deep oxidation of appropriate model compounds containing phosphorus-carbon and sulfur-carbon bonds using the same catalytic system. The result is the first observation of the efficient catalytic oxidative cleavage of phosphorus-carbon and sulfur-carbon bonds under mild conditions, using dioxygen as the oxidant [2].

In addition to the achievements described above, we have unpublished results in several other areas. For example, we have investigated the possibility of using dihydrogen rather than carbon monoxide as a coreductant in the catalytic deep oxidation of substrates. Even more attractive from a practical standpoint is the possibility of using a mixture of carbon monoxide and dihydrogen (synthesis gas). Indeed, experiments indicated that it is possible to substitute carbon monoxide by dihydrogen or synthesis gas. Significantly, in the case of nitro compounds, the deep oxidation in fact proceeded faster when dihydrogen rather than carbon monoxide was the coreductant.

Finally, we have achieved the oxidative degradation and chemical recycling of a wide range of polymeric materials under relatively mild conditions using nitrogen oxides and dioxygen [3]. With the production of polymeric materials on the rise and landfill space at a premium, it becomes increasingly important to develop new techniques for reducing the amount of material lost to the landfill. While some condensation polymers are chemically recycled, there is very little, if any, recycling of addition polymers which constitute 75% by weight of all polymers manufactured. Using our procedure, a wide variety of addition and condensation polymers can be oxidatively

degraded. In the particular cases of polystyrene, high and low density polyethylene and, perhaps, polypropylene useful organics are produced in moderate to good yields.

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2. "The Deep Oxidation of Chemical Warfare Agent Models: Facile Catalytic Oxidative Cleavage of Phosphorus-Carbon and Sulfur-Carbon Bonds using Dioxygen," Terrence Hogan, Robert Simpson, Minren Lin, and Ayusman Sen. Catal. Lett., 1997, 49, 59.
3. "Chemical Recycling of Plastics to Useful Organics by Oxidative Degradation," Anne Pifer and Ayusman Sen. Angew. Chem., submitted.

Planned Activities

We plan to continue our research on new systems for the oxidation of toxic organics and polymers. As described in the original proposal, the research will encompass: (a) the elucidation of the detailed mechanism of oxidation, including the identification of the active species and the nature of the bond-breaking and oxidation steps, and (b) the identification of the classes of organics and polymers that can be efficiently oxidized and thereby removed and/or recycled. The ultimate goal of the research is the design of one or more cleanup systems that would be useful from a practical standpoint. While the design of procedures for removal of organics and polymers from water would be the first priority of research, the use of similar systems for the oxidation of non-aqueous phase organics and polymers will also be investigated.

Evaluation of Isotopic Diagnostics for Subsurface Characterization and Monitoring: Field Experiments at the TAN and RWMC (SDA) Sites, INEL

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Research Objective

This research is aimed at improving methods for characterizing underground contamination sites and for monitoring how they change with time. Particular emphasis is placed on identifying and quantifying the effects of intrinsic remediation, and verifying the efficacy of engineered remediation activities.

Isotopic measurements of elements like C, O, H, He, Cl, and Sr, which are present in groundwater and soil gas, provide a quantitative measure of material balance. They can be used to identify the sites of origin of contaminants in groundwater, and to determine if contaminants are being destroyed as a result of natural processes or engineered processes. Isotope ratios can also be used to trace the migration of fluids that are pumped down wells to destroy or confine underground contaminants,

such as steam and grout, and they can be used to diagnose what chemical reactions are occuring underground and what materials are reacting. For example, destruction of TCE usually produces carbon dioxide, but carbon dioxide can also come from dissolution of calcite.

There are many isotopic ratios that can be measured in groundwater and vadose zone gas that could be valuable for characterizing remediation sites and monitoring remediation activities. We concentrate on a few that are particularly useful for the problems being addressed at the TAN (Test Area North) and RWMC (Radioactive Waste Management Complex) sites of the Idaho National Engineering Laboratory. The isotopes we are using are carbon-13, carbon-14, helium-3, strontium-87, chlorine-37, and oxygen-18.

Research Progress and Implications

This report summarizes work completed after 1.5 years of a 3-year project.

Sampling

Application of the isotopic techniques requires field sampling and the return of the samples to the laboratory for analysis. At RWMC, vadose zone gas samples are obtained routinely for monitoring of CCl_4 and other contaminants. The sampling is done via a series of monitoring wells that surround the site of the buried materials. Wells located relatively far from the burial trenches penetrate to the water table whereas those close to the burial trenches penetrate to about 200 feet depth.

The character of subsurface gas at RWMC varies seasonally and with the operation of the VVE system, so it is necessary to sample the system relatively often to characterize it. A subset of samples from the normal weekly monitoring of RWMC was sent to us at LBNL in November 1996, February 1997, March 1997, and June 1997. The sampling is continuing. A partial set of water samples from TAN groundwater was sent to us in July of 1997, and the remainder of sample set was sent in October 1997. The TAN groundwater plume evolves at a much slower timescale than the RWMC vadose zone plume, so sampling needs to be done only a few times during the course of the study.

Measurements

The RWMC gas samples have been measured for $^{13}C/^{12}C$ ratios, $^{14}C/^{12}C$ ratios, and the concentrations of CO_2, O_2, and N_2. Noble gas concentration and isotopic analyses are planned but have not yet been carried out. TAN water samples have so far been measured for $^{13}C/^{12}C$ ratios, $^{18}O/^{16}O$ ratios, D/H ratios, the concentration of dissolved inorganic carbon (DIC) and selected anions and cations, and $^{87}Sr/^{86}Sr$ and $^{14}C/^{12}C$ ratios.

Results

1) There is substantial production of CO_2 in the subsurface of the RWMC site. This production is far above the background values that can be observed outside from the Subsurface Disposal Area (SDA). The vadose zone CO_2 has a low $^{13}C/^{12}C$ ratio and therefore appears to be an oxidation product of organic material. It is not yet possible to determine with confidence which organic material is being oxidized and by what mechanism, but our preliminary assessment is that the source of the CO_2 is oxidation of the lubricating oil rather than oxidation of the chlorinated solvents.
2) Initial ^{14}C analyses of the CO_2 indicate the presence of an additional, radioactive source for the CO_2 in the vadose zone of RWMC. This source is tentatively identified as buried reflector blocks from nuclear reactors. Evidence of migration of the ^{14}C is found in the “background” monitoring well about 1 km southeast of the trenches.
3) A map of the $^{18}O/^{16}O$ and D/H values of groundwater at TAN indicate a region near and to the south of the injection well that has relatively high $^{18}O/^{16}O$. These waters also have D/H values that indicate they have been subject to evaporation. These isotopic data indicate a significant contribution of evaporated water, presumably from the TSF-07 disposal pond.
4) The $^{13}C/^{12}C$ values of TAN groundwater DIC are 2-3‰ lower in the vicinity of the plume, indicating a possible contribution from degradation of contaminants.

5) Analysis of $^{87}Sr/^{86}Sr$, $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in TAN groundwater from below the lower confining layer of the upper aquifer indicates that the waters below and above the layer have distinct isotopic signatures, which confirms that there is no exchange across the lower confining layer.
6) The contaminant plume water has a traceable signature for $^{87}Sr/^{86}Sr$; comparison of the plume as represented by the Sr isotopic data and the distribution of TCE may yield information on the amount of in-situ degradation in the plume.

Implications

The results to date confirm that isotopic analysis of groundwaters and vadose zone gases are useful for diagnosing chemical processes occurring in the subsurface, and tracing the migration of waters from different sources. At both the RWMC and TAN sites there is evidence of biodegradation of organic material in the subsurface, although the evidence to date suggests that the most problematic contaminants are not being degraded at a significant rate. This needs to be confirmed with more analytical work and modelling.

Planned Activities

Over the next year, sampling and analysis of vadose zone gases and groundwaters will continue. At RWMC the objective will be to discern any changes with time, and to better charaterize seasonal variations. There will also be an effort to measure samples of shallow soil gas. A set of measurements will also be made in conjunction with a tracer test in June 1998. AT TAN an additional set of samples will be measured for $^{87}Sr/^{86}Sr$, $^{13}C/^{12}C$, $^{14}C/^{12}C$, $^{18}O/^{16}O$, and D/H; partly to confirm the data from the first sampling and also to extend the coverage to wells outside the immediate area of TAN. AT both RWMC and TAN, samples of chlorinated hydrocarbons will be measured for $^{37}Cl/^{35}Cl$ and $^{13}C/^{12}C$ as a direct means of assessing the effects and extent of natural degradation.

Aquifer Transport of Th, U, Ra, and Rn in Solution and on Colloids

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Research Objective

The investigation focuses on understanding the behavior of naturally occurring U, Th, Ra, and Rn isotopes in groundwater along with the supply rates of these isotopes by rock alteration, and utilizing these species as natural analogues for waste radionuclides, thereby providing a basis for predicting contaminant migration behavior in potentially impacted aquifers. The study examines the fundamental controls on natural radionuclide transport in specific aquifers by integrating aquifer sample analyses, focussed laboratory experiments, field observations, and theoretical modeling.

Research Progress and Implications

The study approach has been to select a reasonably well-characterized aquifer related to a DOE site where groundwaters can be readily collected for analysis of the diverse range of U- and Th-series nuclides and major element chemistry. The field studies to date have focussed on the sandy unconfined aquifer underlying DOE's Brookhaven National Laboratory on Long Island, N.Y., where substantial hydrogeological information is available and where an extensive groundwater monitoring network had been established previously. Groundwater samples were collected from a series of monitoring wells of various depths and nominally along flow paths. Filtration and ultrafiltration techniques

were used to concentrate colloids and particles. Samples were analyzed for major element chemistry, short-lived nuclide concentrations by counting techniques and long-lived nuclide concentrations by mass spectrometry.

Significant U concentrations were found at the water table, indicating that substantial amounts of U are supplied to waters percolating through the vadose zone. U concentrations in the aquifer increase and then decrease with distance from the recharge area. Large U isotopic shifts occur in the groundwaters below the water table, while moderate ^{234}U enrichments are generated within the vadose zone. Colloids >10k Daltons account for 40-75% of the U in the aqueous phase and are clearly important carriers of U. The concentrations of dissolved ^{232}Th are ~3 orders of magnitude lower than those of ^{238}U in the groundwaters, and are close to the predicted thorianite solubility for each sample pH. The amounts of ^{222}Rn in the water represent 4-20% of the Rn produced in the rock by decay. Where the dissolved ^{226}Ra concentrations are lower, the dissolved Rn concentration is generally greater, suggesting that higher Rn concentrations in the water are due to increased amounts of ^{226}Ra on surfaces of the aquifer rock. The activities of the three Ra isotopes are generally comparable to one another in the groundwaters throughout the aquifer and exhibit variations are not systematic but follow those of Ba and appear to be related to groundwater pH. Therefore, sorption processes likely exerts a strong control on dissolved Ra concentrations.

As a guide to interpreting the analytical results, a simple theoretical model has been developed for the transport of U, Th, Ra, and Rn in the vadose zone above the water table and within the aquifer. The model treats the aquifer as three phases: the groundwater; the rock consisting of large grains typical of the aquifer mineralogy and small minor phases in which radioactive elements are concentrated; and a surface layer coating the grains that is available for physico-chemical reactions. The model explicitly considers: transport of radionuclides by advection; physico-chemical exchanges between the groundwater and the reactive surface; and supply of radionuclides by weathering of primary phases and recoil from decay of parent nuclides within aquifer solids. Diffusive transport and lateral mixing are not considered. Self-consistent, one-dimensional equations were developed for the evolution of the radionuclide concentrations in waters percolating through the vadose zone and flowing within the aquifer. Solutions have been obtained for the case where U in the groundwater does not react with the aquifer solids and Th and Ra are highly surface-reactive, and the evolution of the concentration of these elements along a flow path have been calculated.

A reasonable and consistent set of results have been obtained for general solutions to the model. For groundwater U concentrations and isotopic compositions comparable to those measured in the Long Island aquifer, the model yields weathering rates for the vadose zone that are somewhat higher than those of the aquifer. These rates are consistent with the range of published laboratory results. Rates of release of ^{234}Th by recoil during decay of parent ^{238}U that are calculated by the model are consistent with the concentration of U in minor phases within the aquifer solids. These release rates are several orders of magnitude smaller than those obtained for ^{222}Rn, indicating that Rn release rates cannot be directly applied to all other radionuclides in the decay series, as previously suggested in the literature. Observed decreases in groundwater U concentration with increasing distance are not accounted for by the model; either U is removed by reaction with surfaces or the sampling locations are not along a flowline. Fluctuations in ^{234}Th and Ra isotope concentrations as well as U isotope compositions cannot be accounted for by model conditions that assume a uniform aquifer, and require variations in aquifer parameters. Major element and radionuclide data indicate that at least one well shows the influence of mixing with water from the underlying aquifer, indicating that the study aquifer is not completely isolated.

Planned Activities

Further work on the Long Island aquifer in 1998 will include additional sampling to characterize the extent of variability of groundwaters at the water table and between flowlines in the unconfined aquifer, relating the results obtained in this study to available information regarding migrations of other contaminants at the site, and evaluating the possible effects of inflows of water into the aquifer from the underlying deposits. We will increase interactions with the hydrologists at Brookhaven to further integrate the study results with known hydrologic information.

Laboratory experiments are planned for the next year to identify the rates of release of radionuclides from aquifer solids. Initial experiments will examine the controls on the release of ^{222}Rn from specific radioactive minerals and bulk aquifer solids. Techniques will then be developed to determine the release rates of Th, U, and Ra isotopes. In order to apply the results to aquifer data, measurements will be made on the distribution of radionuclides in specific mineral phases, surface coatings, and leachable sites in aquifer solids.

The work to date has identified the vadose zone as a significant source of radionuclides to the groundwater based on measurements of very shallow groundwaters. Sampling is planned for late 1998 to collect waters from different levels within the vadose zone above one of the aquifer study sites. The concentrations of radionuclides in percolating waters and the distribution of radionuclides in soil solids will be determined. This data will be used to further characterize the mechanisms of radionuclide supply from soil solids, the interactions of radionuclides in percolating waters with solid surfaces, and the rates of radionuclide vertical migration from the surface and into the groundwater.

A sampling program of a second aquifer will be conducted in 1999 to consider radionuclide migration under different aquifer conditions. The well-characterized Edwards aquifer, which supplies water to San Antonio in south-central Texas, is within a limestone that contains both oxic and anoxic conditions and can be readily sampled. Analyses of groundwaters of various ages and chemistries, as well as of core samples that have been obtained from the USGS, are planned. Another aquifer being considered for study is the Great Artesian Basin in Australia, where samples can be collected from the limited recharge areas and along long flow paths in confined layers. Here, it can be determined whether continuous weathering processes continue to add 'conservative' nuclides (e.g., ^{234}U and ^{238}U) over long flow distances.

Efforts will continue in refining the theoretical framework for understanding radionuclide migration from the surface through the vadose zone and in aquifers under a range of conditions. This will include further developing the present model to include interaction of U with aquifer surfaces, to explicitly incorporate the behavior of colloids, and to include the effects of lateral mixing between flow paths.

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The Migration and Entrapment of DNAPLs in Physically and Chemically Heterogeneous Porous Media

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Research Objective

The migration and entrapment of dense nonaqueous phase liquids (DNAPLs) at hazardous waste sites is typically believed to be controlled by physical heterogeneities. This belief is based upon the assumption that permeability and capillary properties are determined by soil texture. These transport properties however, also depend on porous media wettability characteristics, which may vary spatially in a formation due to variations in aqueous phase chemistry, contaminant aging, and/or variations in mineralogy and organic matter distributions. The overall objective of this research is to investigate the influence of such coupled physical and chemical heterogeneities on the migration and entrapment

of DNAPLs in the saturated zone. This research includes laboratory and numerical investigations for a matrix of organic contaminants and solid media encompassing a range of wettability characteristics. Specific objectives include: (1) quantification of system wettability and interfacial tensions; (2) determination of transport property relations; (3) two-dimensional infiltration experiments; (4) modification of a continuum based multiphase flow simulator to account for physical heterogeneity, saturation independent and saturation dependent wettability, and concentration dependent wettability and interfacial tension; and (5) utilization of this model to explore the potential influence of coupled physical and chemical heterogeneities on the migration of DNAPLs and the development of innovative remediation schemes. The accomplishment of the above research objectives will facilitate the characterization and remediation of contaminated field sites.

Research Progress and Implications

This section summarizes research conducted towards the accomplishment of goals (1), (2), (4), and (5) during the first 1.5 years of this 3-year project. Goal (3) builds upon results from the other objectives and will be initiated in the coming year.

To address objective (1), a series of experiments have been conducted for xylene-water-quartz systems using the representative surface-active agents, dodecylamine (DDA) and octanoic acid (OA). DDA and OA exhibit pH dependent acid-base speciation in aqueous solution, which results in aqueous chemistry-dependent interfacial tension and/or wettability in these systems. When the neutral species of DDA (pH > 10) and OA (pH < 5) prevailed, minimal changes were observed because of preferential partitioning of DDA and OA into the NAPL. In contrast, the cationic form of DDA (pH < 10) sorbed both to quartz which altered the wettability from water-wet to neutral and to the NAPL-water interface. The anionic form of OA (pH > 5) sorbed only to the NAPL-water interface which lowered the interfacial tension by as much as 50%. Results from these studies will facilitate the quantification of aqueous phase chemistry effects on DNAPL migration and remediation.

To address (2), capillary pressure relations have been measured for a representative DNAPL (tetrachloroethylene), water, and synthetic and natural fractional wettability porous medium systems using a modified pressure cell apparatus. Results indicate that as the organic-wet fraction of a soil increases, for a given saturation and saturation history, the residual water saturation increases and the organic liquid-water capillary pressure decreases, becoming negative during imbibition. Work has also been directed towards the design and construction of an automated apparatus to measure the hydraulic property relations on a number of columns in parallel. Construction is now complete and experimental protocols have been established for its operation. Equilibrium liquid pressure and saturations measured with this apparatus will yield capillary pressure relations, whereas transient outflow measurements will be used to determine the relative permeability relations, in conjunction with history matching procedures. The multiphase flow simulator discussed below has been successfully coupled with a nonlinear least-squares fitting routine for this purpose. Research to address (2) will lead to the development of improved methods to predict, model, and economically measure hydraulic property relations which are required by multiphase flow and transport simulators.

Considerable progress has been made towards the accomplishment of goals (4) and (5). A two-dimensional multiphase flow simulator has been modified to account for coupled physical and chemical aquifer heterogeneity. Saturation independent and saturation dependent wettability effects on the hysteretic hydraulic property relations are currently included, but the simulator does not yet account for concentration dependent wettability and interfacial tension. The implemented hydraulic property model and available experimental data suggest that, for a given saturation and saturation history, increasing the contact angle or organic-wet fraction of a porous media tends to: (1) decrease the organic-water capillary pressure; (2) decease the organic relative permeability; (3) decrease the amount of organic entrapped by water; (4) increase the water relative permeability; and (5) increase the amount of organic retained as an immobile film coating solid surfaces. This simulator has been employed to investigate the potential influence of coupled physical and chemical heterogeneity on DNAPL flow and entrapment. For reasonable ranges of wettability characteristics, simulations suggest that spatial variations in wettability can have a dramatic impact on DNAPL distributions. In physically homogeneous systems, increasing the contact angle or organic-wet fraction of a soil produces a

prolonged slow migration of the DNAPL creating larger contaminated aquifer regions with lower organic saturations. In coupled physically and chemically heterogeneous systems, interfaces of capillary property contrast (soil texture or soil wettabilities) lead to higher organic saturations, increased lateral spreading, and decreased depths of organic liquid infiltration.

Planned Activities

Future work will investigate whether OA and DDA have a similar effect on interfacial properties when tetrachloroethylene is the NAPL. Experimental research efforts will also focus on the determination, quantification, and prediction of capillary and relative permeability relations for variously wetted synthetic and natural porous media. Results from these studies will be utilized in the development and design stages of the two-dimensional organic liquid infiltration experiments which will be initiated this year. Numerical modeling efforts will initially be directed towards the simulation of transient outflow experiments (to determine the relative permeability relations), and then two-dimensional infiltration experiments. Modifications to the simulator to account for concentration-dependent interfacial tension and wettability will be made as information and insight is gained from the above mentioned experiments.

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Partitioning Tracers for In Situ Detection and Quantification of Dense Nonaqueous Phase Liquids in Groundwater Systems

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Research Objective

The overall goal of the proposed project is to explore the use of an innovative in-situ method for the detection and quantification of dense nonaqueous phase liquids (DNAPLs) in water-saturated and unsaturated heterogeneous media. Effective risk assessment and remediation of DNAPL contaminated sites is constrained by the limitations of current site characterization techniques. A major weakness of the current methods is that they provide data at discrete points, such that the probability of sampling a zone of localized DNAPL is quite small. The results of the proposed research will lead to improved techniques for characterizing DNAPL contaminated sites and will enhance our understanding of the distribution of DNAPLs in the subsurface. The use of this methods will reduce the uncertainty associated with risk assessments and remediation planning. The project objectives include exploring partitioning tracers for the detection and quantification of DNAPLs in saturated systems using aqueous tracers and in unsaturated systems using gas-phase tracers.

Research Progress and Implications

This report summarizes work completed mid-way through year 2 of a 3-year project. Batch experiments have been conducted for a suite of bulk-phase partitioning tracers to determine water-trichloroethene (TCE) partitioning coefficients. Interfacial tension measurements have been made between TCE and solutions of several potential interface partitioning tracers. Preliminary column experiments have been conducted for the aqueous bulk-phase partitioning tracers using columns packed with a homogeneous sand and containing a residual saturation of TCE. These preliminary sets of experiments have enabled selection of suitable tracers for the water-saturated experiments and have lead to improved experimental designs and methods.

To conduct detailed, quantitative tracer studies at the intermediate scale, we've designed and constructed a new flow cell. The inside dimensions are 1.8 x 1 x 0.05 m. The flow cell is designed to be fully compatible with our dual-energy gamma radiation system. With that system, we intend to measure water and residual NAPL saturation simultaneously. One side of the flow cell is made of glass, to allow flow and transport visualization. The other wall is made of Kynar, a DNAPL resistant plastic. The Kynar wall has been machined to allow for the installation of twenty-four point-sampling ports consisting of laser drilled stainless steel tubing. Depth integrated sampling ports have also been installed. An automated sampling system has been designed and will soon be installed. Preparations have been made for packing the flow cell. Arrangements have been made with EMSL (Environmental Molecular Sciences Laboratory) for the analysis of TCE and our four tracers TCE using GC-MS, LC-MS, and an Ion Chromatograph.

Batch experiments have also been conducted for a suite of gas-phase partitioning tracers to determine their Henry's Constants and air-NAPL partition coefficients. Preliminary gas transport experiments have been conducted for the gas-phase partitioning tracers using columns packed with a homogeneous sand and containing a residual saturation of water. Results from these preliminary

sets of experiments will be used to help in the selection of suitable tracers for the unsaturated experiments and have improved experimental designs and methods.

We have tested the gas-phase partitioning tracer method in a controlled field-scale experiment conducted in a large weighing lysimeter located at the University of Arizona's Karsten Center for Research. The lysimeter is 4.0 m deep, 2.5 m in diameter, and is equipped with tensiometers, TDR probes, a neutron-probe access tube, and 48 porous stainless steel cups for gas injection and sampling. The weighing scales have a capacity of 45 Mg and can detect a 200-g mass change, equivalent to ± 0.04 mm of water on the surface. The instrumentation allows the values of water content estimated from the partitioning tracer experiment to be compared to known values obtained with the neutron probe. Pressure transducers (model 136PC15G2, Microswitch, Freeport, IL) installed at 50 cm increments from the inlet allow pressure to be monitored during the tracer experiments. The lysimeter was filled homogeneously with Vinton fine sand (sandy, mixed thermic Typic Torrifluvent). To date, we have tested the method for measuring water content. In the future, we will inject TCE-NAPL in the lysimeter and test the gas-phase partitioning tracer method for measuring TCE-NAPL in an unsaturated system.

Our results to date demonstrate that the lysimeter provides a well-controlled setting for exploring the use of gas-phase tracer tests for measuring immiscible liquid saturations. Our results indicate that tracer tests have the potential to accurately measure water contents at the field scale. This method would complement both the traditional, small-scale methods and the regional [watershed] scale methods of measuring water content.

The performance of the STOMP simulator to compute multiple-phase flow through subsurface environments was improved for conditions of nonwetting fluid entrapment. The original version of the STOMP simulator modeled nonwetting fluid entrapment and scanning path hysteresis using the relative permeability-saturation-capillary pressure (k-s-p) theory developed by Lenhard and Parker (1987 Water Resources Research). This simplified model of Kaluarachichi and Parker, including air entrapment for three-phase cases, has been incorporated into the Water-Air and Water-Oil-Air operational modes of the STOMP simulator and is currently being verified for proper execution.

Planned Activities

Summer 1998: Bulk-phase partitioning tracer experiments will be conducted in saturated columns containing TCE-NAPL at different pore-water velocities to test the effect of rate-limited mass transfer. Also the form and quantity of NAPL will be varied. In addition, experiments will be conducted in the intermediate-scale flow cell. The STOMP simulator will continue to be modified and tested.

Fall 1998: Experiments will be conducted to examine the transport of interface partitioning tracers in saturated systems containing NAPL. Gas transport experiments will be conducted in the weighing lysimeter to measure NAPL saturation. Data collected from experiments conducted in the flow cell during the summer will be analyzed. The STOMP simulator will continue to be modified and tested.

Spring 1999: The STOMP simulator will be used to simulate data collected from experiments conducted in the flow cell. These results will be compared to other models.

Physics of DNAPL Migration and Remediation in the Presence of Heterogeneities

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Research Objective

The goal of our research is to develop a fundamental quantitative understanding of the role of physical heterogeneities on DNAPL migration and remediation in aquifers. Such understanding is critical to cost effectively identify the location of the subsurface zone of contamination and design remediation schemes focused on removing the source of the contamination, the DNAPL itself. To reach this goal, the following objectives for the proposed research are defined:

Objective 1: Develop fundamental understanding of the physics of DNAPL migration processes within heterogeneous porous media: a) Conduct a suite of two-dimensional thin slab physical experiments within controlled and systematically varied heterogeneous porous media at scales up to one meter. Vary system parameters to consider a range of capillary and bond numbers within these heterogeneous porous structures. b) Develop a new DNAPL migration model based on an Up-scaling of Invasion Percolation (UIP) to model the migration process. Compare the model predictions to experimental results. Accomplishing objective 1 provides a series of experiments against which we will be able to evaluate the validity of existing multi-phase flow theory as formulated in both percolation codes and in continuum flow codes. These experimental results will also provide new insights into DNAPL migration behavior. Development of the UIP model will provide an exciting alternative to continuum multi-phase flow codes since UIP offers several advantages for modeling DNAPL migration. The UIP model is fast, allowing for: 1) modeling in three dimensions; 2) the incorporation of much more geologic detail; and, 3) its use in probabilistic modeling by way of Monte Carlo techniques. In addition, the UIP code requires much less input data and it can handle density-driven fingering, a process known to occur with DNAPLs.

Objective 2: Develop fundamental understanding of the physics of DNAPL remediation processes within heterogeneous porous media: Conduct a suite of physical experiments within controlled and systematically varied heterogeneous porous media at scales up to one meter that consider surfactant and alcohol flushing and possibly air sparging remediation treatments. Accomplishing objective 2 will allow us to consider the efficacy of several promising DNAPL remediation techniques under realistic yet well-controlled conditions. We consider this work to be of the type of broad-based, initial studies needed to better understand the intricacies associated with various remedial processes. We expect that the results of this work will be used to focus subsequent research on those remedial approaches or combination of approaches that appear to offer the most promise.

Research Progress and Implications

This report summarizes work after 21 months of a 36-month project.

Objective 1: Develop fundamental understanding of the physics of DNAPL migration processes within heterogeneous porous media.

Our approach integrates experimentation using unique capabilities at SNL's Flow Visualization and Process Lab with development of new approaches for modeling DNAPL migration. Our experimental system consists of a 2D, sand-filled, initially water-saturated chamber (60cm high, 30cm wide, 1cm thick) where we can fully visualize DNAPL migration using light transmission techniques. Image analysis tracks the differences in light intensity for each successive image thereby

yielding a time series of the displacement process at exceptional spatial and temporal resolution. Such resolution allows us to perform detailed data analysis that is sufficient to increase our understanding of DNAPL migration processes and to test our upscaled percolation model. In order to make reproducible geologic structures for our experiments we use a unique computer-controlled sand-filling apparatus. With our filler we can make macro heterogeneities (such as discrete formation-scale features like facies) as well as smaller scale micro heterogeneities (such as micro layering and crossbedding found within lithologic units).

Our percolation model neglects viscous forces. DNAPL migration is entirely dictated by local capillary and gravity forces as applied at scales on the order of centimeters. Percolation models simply track growth order (instead of solving for a pressure field at each time step) resulting in very fast computations. The speed of the model allows much more detail about heterogeneities to be incorporated. The UIP model easily models gravity driven fingering, a process common to DNAPL migration. Data requirements for the UIP model are light and readily obtainable. All that is needed is DNAPL density and interfacial tension, and the boundaries of lithologic units and their textures.

In macro-heterogeneous fields, we have conducted a suite of immiscible displacements through heterogeneous porous media in which we vary system parameters to consider DNAPL migration over a range of capillary and Bond numbers. All our experiments clearly show the invasion field to evolve in a series of gravity stabilized and destabilized invasion periods resulting in a final configuration of fingers and pools. We also have discovered pulsation within the flow field and the formation of multiple fingers even at low capillary numbers. These phenomena are important as they can result in more complicated migration behavior. With the exception of these effects, our UIP modeling shows good agreement to experiment even for increases in capillary number of over 2 orders of magnitude. The implication of these encouraging results is that the negligible viscous effect assumption in the percolation model will probably not be violated for the vast majority of DNAPL spill situations.

We have also begun to explore the effects of micro heterogeneities (such as micro layering and crossbedding found within lithologic units). In an initial series of experiments, microstructures have been varied through their “intensity” in terms of property variation across individual laminae. Results obtained suggest that the degree of small-scale heterogeneities affect effective block saturations and may well affect accessibility rules for the upscaled percolations. Additionally, in these laminated systems we see that effective block saturations are much more sensitive to flow rate than in either homogeneous systems or in discrete/macro-scale systems that we have studied. Percolation modeling of these experiments is in progress.

Additionally, a set of UIP enhancements are under consideration for: 1) the simultaneous invasion of both wetting (water) and non-wetting (DNAPL) phases (rudimentary model currently implemented); 2) incorporation of viscous forces (multiple fingers and greater “fill in” of migration field); and 3) dynamic time-varying contact angles.

Objective 2: Develop fundamental understanding of the physics of DNAPL remediation processes within heterogeneous porous media.

Simulators of remediation processes have not been extensively tested, in part due to the general lack of results from controlled experiments. Verified simulators of remediation processes are sorely needed as remedial selection and design tools. And since sufficient geologic detail is almost always lacking, it is important to understand the errors introduced through paucity of geologic detail.

Through our work on DNAPL migration, we have developed a unique experimental system where we can reproduce complicated heterogeneity structures. This system also allows us to conduct experiments for the first time that can compare several competing approaches for DNAPL remediation on equal footing. The combination of DNAPL migration studies and DNAPL remediation studies is also critical in that we can provide realistic initial DNAPL emplacement conditions for the remediation experiments. We emplace the DNAPL through a migration experiment as performed within the context of objective 1, followed by a remediation experiment.

We have completed construction of a 60cm x 60cm chamber required to run the remediation experiments. Design and construction of this chamber was complicated by the weight of the chamber and the additional ports required to run the remediation experiments. We have established a protocol - explicit, detailed procedures - for conducting these remediation experiments. We have purchased

a gas chromatograph to measure effluent concentrations from the experiments and expect to run our first remediation experiment - surfactant solubilization - in the July/August 1998 time frame.

We intend to work closely with developers of each remediation approach to attempt to optimize the remedial process and show each technique in its best possible light. These experiments will be extremely useful to the remediation developers in helping them understand the physics and chemistry of their remediation processes as they perform under more realistic, less idealized, conditions. Toward that end, Alex Meyer, a professor at Michigan Tech, visited our lab and is collaborating with us on our first series of experiments looking at surfactant mobilization and solubilization of DNAPLs.

Planned Activities

We are in the process of completing data analysis and percolation modeling of all our DNAPL migration experiments. Through the end of this calendar year, we will be writing papers describing our research results.

This Summer we begin running our remediation experiments. We expect to continue running remediation experiments through the Spring of 1999 and write a series of papers describing results through the end of our funding in September 1999.

We anticipate funding beginning in FY 1999 from EM-50's Subsurface Contamination Focus Area for the purpose of conducting an extensive field application of our upscaled percolation modeling approach for locating DNAPLs. This funding will help provide the link from the basic science we have been performing in the EMSP to wide-spread application at DOE field sites.

Other Access To Information

Visit our web site at **http://www.nwer.sandia.gov/flowlab**

We have completed a paper that describes how our upscaled percolation model can be used within a Monte Carlo analysis to help determine DNAPL location by creating a probability map of where the DNAPLs might reside. Such a map could be used in conjunction with any DNAPL detection technology to suggest the most profitable sampling locations. Contact us to receive a copy. The citation is:

Borchers, B., S.H. Conrad, E.K. Webb, R.J. Glass Jr., R. Cox. 1997. A simulation and decision analysis approach to locating DNAPL in subsurface sediments. Sandia Report SAND97-2261.

In Situ, Field Scale Evaluation of Surfactant Enhanced DNAPL Recovery Using a Single-Well, Push-Pull Test

Jonathan D. Istok, Oregon State University

Research Objective

The overall goal of this project is to develop the single-well, "push-pull" test method as a new site characterization and feasibility assessment tool for studying the fundamental fate and transport behavior of injected surfactants and their ability to solubilize and mobilize dense nonaqueous phase liquids (DNAPLs) in the subsurface. The specific objectives are:

(1) to develop a modified "push-pull" test for use in identifying and quantifying the effects of sorption, precipitation, and biodegradation on the fate and transport of injected surfactants,

(2) to use the developed test method to quantify the effects of these processes on the ability of injected surfactants to solubilize and mobilize residual phase trichloroethylene, and
(3) to demonstrate the utility of the developed test method for performing site characterization and feasibility studies for surfactant enhanced DNAPL recovery systems.

Research Progress and Implications

This report summarizes work as of June 1, 1998 (after 20 months of a 36-month project); laboratory and field work as been successfully completed for all three objectives.

The ability of the push-pull test method to characterize sorption of linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactants to natural aquifer sediment was evaluated using sediment and groundwater from a TCE contaminated field site at the Building 834 operable unit at Site 300, Lawrence Livermore National Laboratory. Sorption isotherms exhibited Langmuir-type behavior with larger apparent sorption maximums for LAS than for DOWFAX. Laboratory push-pull tests were performed in unique intermediate-scale physical aquifer models (flow cells) designed and operated to approximate the radial flow field around an injection/extraction well during a field push-pull test. The models were packed with aquifer sediment from the same aquifer unit used in field push-pull tests. Results of laboratory push-pull tests indicated substantial retardation and chromatographic separation of injected LAS, but no apparent retardation or separation of injected DOWFAX. Experimental results and numerical modeling indicate that LAS and DOWFAX sorption may be kinetically-limited during transport. Field push-pull tests were successfully completed in monitoring wells D-6 and D-12, which are close to the TCE source zone but do not contain residual TCE. In these tests, 50 L of surfactant solution containing a bromide tracer were injected into the saturated zone at a depth of ~ 8 m. During the extraction phase, 100 L of test solution/groundwater mixture were extracted and analyzed for tracer, surfactant, and TCE. The field results confirmed the ability of the push-pull test method to rapidly characterize surfactant sorption to aquifer sediments in-situ. Field tests were conducted in collaboration with LLNL personnel and the EMSP project “Development of radon-222 as a natural tracer for monitoring the remediation of NAPL contamination in the subsurface”. This allowed an independent determination of residual TCE saturation in the vicinity of the monitoring wells during each test.

As part of this work, a simplified method was developed for estimating retardation factors from push-pull test results by comparing extraction phase breakthrough curves for solutes undergoing linear equilibrium sorption and a nonsorbing tracer. Using numerical simulations an extensive sensitivity analysis was performed to test the method’s performance for several cases, including push-pull tests conducted in homogeneous and heterogeneous (layered) aquifers, as well as tests conducted in wells screened across the entire saturated thickness and wells in which a packer system is used to isolate a portion of the aquifer. The simplified method proved useful in estimating retardation factors for all cases except under conditions of severe heterogeneity.

The ability of the push-pull test method to characterize surfactant enhanced solubilization of residual TCE by DOWFAX was also evaluated using sediment and groundwater from Site 300. Batch solubilization experiments indicated a linear relationship between TCE solubility and DOWFAX concentration characterized by weight- (WSR) and molar solubilization ratio (MSR) of 0.26 and 1.25, respectively. Laboratory push-pull tests were performed in physical models with both TCE-free sediment and in sediment containing 920.2 g TCE, which corresponded to a residual saturation of 5 vol. % of the pore space. In push-pull tracer tests conducted in the absence of DOWFAX, maximum aqueous phase TCE concentrations were ~ 500 mg/L. In contrast, during the first push-pull test conducted with 13,500 mg/L active DOWFAX, aqueous phase TCE concentrations increased to ~ 3,000 mg/L and TCE mass recovery increased by a factor of ~ 3. Successive push-pull tests conducted with DOWFAX yielded decreasing TCE recovery, such that by the third experiment no increase in TCE recovery was obtained. Excavation of the sediment pack confirmed the quantity of residual TCE removed by surfactant and indicated that no mobilization of residual TCE had occurred. As part of this work a novel analytical method was developed for determining TCE concentrations in the presence of large concentrations of anionic surfactants. The method uses high performance liquid chromatography with photodioide array detection to allow detection of TCE (for concentrations greater than ~ 0.1 mg/L) and surfactant by the direct injection of a single

aqueous sample and substantially reduces the costs of laboratory and field experiments. Laboratory push-pull tests were conducted in collaboration with the EMSP project "Development of radon-222 as a natural tracer for monitoring the remediation of NAPL contamination in the subsurface". Measurements of dissolved radon-222 gas were used to quantify the spatial reduction in residual TCE saturation following each push-pull test with DOWFAX.

Implications

As a result of this project, the push-pull test method is ready for field deployment at any site where the use of surfactant enhanced DNAPL recovery is being considered. The method is performed in-situ using existing monitoring wells, without the need for core collection. Quantitative information on surfactant sorption or residual DNAPL solubilization potential can be obtained in only one day of field work at most sites. Because the method greatly reduces site characterization and feasibility assessment costs it should substantially reduce the time and cost of remedial action at contaminated sites.

Planned Activities

Additional experiments are in progress to characterize residual TCE solubilization by a third surfactant, Aerosol MA80-I (sodium dihexylsulfosuccinate). To produce a neutrally-bouyant injection solution, 4 wt % Aerosol MA80-I will be combined with 10% isopropanol and 0.32 wt % potassium bromide. Push-pull experiments will be conducted in physical aquifer models packed with sediment obtained from LLNL Site 300 in the presence and absence of added TCE. The effect of cation exchange between the injected sodium/potassium surfactant solution and sediment-associated calcium on the phase behavior of the surfactant and its ability to solubilize TCE will be investigated.

Other Access To Information

The following manuscript preprints are available from Dr. Istok:

Istok, J.D., J.A. Field, M.D. Humphrey, T.E. Sawyer, and M.H. Schroth. 1998. Laboratory and field investigation of surfactant sorption using single-well, "push-pull" tests. Submitted to Ground Water.

Field, J.A., J.D. Istok, M.D. Humphrey, T.E. Sawyer, and M.H. Schroth. 1998. Laboratory investigation of surfactant-enhanced TCE solubilization using single-well, "push-pull" tests. Submitted to Ground Water.

Field, J.A. and T.E. Sawyer. 1998. HPLC method for simultaneous determination of TCE and anionic surfactants at high surfactant concentrations. Submitted to Journal of Chromatography.

Schroth, M.H., J.A. Field, R. Haggerty, M.D. Humphrey, and J.D. Istok. 1998. In-situ evaluation of solute retardation using single-well push-pull tests. Submitted to Journal of Hydrology.

Behavior of Dense, Immiscible Solvents in Fractured Clay-Rich Soils

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Research Objective

This research project addresses the nature and and distribution of DNAPL sources (typically chlorinated solvents) in fractured clays or shales and the potential for natural attenuation of plumes derived from these sources. Specific goals include: 1) determining whether typical DNAPLs can penetrate fractures and the fine-grained matrix pore structure for head values within the range expected for a typical DNAPL spill; 2) investigate methods of measuring or estimating fracture or matrix entry pressure and pressure-saturation curves for these materials; 3) experimentally determine whether DNAPL residuals in fractures can be significantly depleted by dissolution and diffusion into the fine-grained matrix over the time-frame relevant to many contaminant investigation and remediation programs; and 4) assess potential for natural attenuation of common DNAPLs (TCE and its degradation products) in these deposits. Preliminary investigations indicate that DNAPL source removal will be a much more difficult and slower process for fractured clay-rich deposits than for granular deposits. These basic research investigations are needed to build the scientific framework for assessment of remediation options or for determining whether remediation, at least for the source zone, should be considered Technically Impractible (TI).

Research Progress and Implications

This report summarizes progress made during the first 1.7 years of a 3-year project. The project investigates the behavior of DNAPLs in two fractured clay-rich materials: weathered shales at Oak Ridge National Lab. in east Tennessee; and weathered glacial till in southern Ontario. The materials, although very different in origin, are similar in terms of fracturing, porosity and hydraulic conductivity and DNAPLs are expected to behave in similar fashions in the two materials. This allows the researchers to share their expertise, as well as helping to determine whether the findings of these studies are applicable to a broader spectrum of fractured clay-rich materials. Results to date for the major sub-projects are briefly described below:

Weathered and Fractured Shale Column Experiments

Air/water and DNAPL/water entry and pressure-saturation curves have been experimentally measured for an undisturbed column sample of fractured weathered shale from Oak Ridge National Laboratory (ORNL). The DNAPL used for the experiments was a non-hazardous compound manufactured under the trade name Fluorinert FC-40. Preliminary evaluation of the results indicate that air/water data can be used, along with appropriate scaling factors based on the differences in fluid properties, to estimate DNAPL behavior. This is significant, because it raises the possibility that field scale air/water measurements could be used as a non-hazardous means of predicting DNAPL/water relationships. At capillary pressure head values of 5-8 cm the DNAPL first entered the fractures and at 160-210 cm it began to enter the fine-grained matrix. These are well within the range of head values expected for even a small DNAPL spill, so it indicates that at many sites DNAPL is likely to

enter both the fractures and the matrix. Investigations of pore size distribution using mercury porosimetry indicate that pore-throat sizes range from 3 nm to 8000 nm, which are smaller than the maximum size indicated by the column experiments, but this is likely related to the small size of the samples used for porosimetry.

DNAPL Natural Attenuation Field Site in Shale and Weathered Shale

A field facility at the Oak Ridge National Laboratory is serving as an extraordinary example of how natural attenuation processes can reduce the off-site transport of chlorinated organics in a fractured and slightly weathered shale. The field facility consists of a 35 m long transect of multilevel sampling wells located in a discharge zone adjacent to existing waste trenches that contain organic contaminants. The wells indicate the presence of a fast flowing fracture regime and a fine-grained matrix regime with very slow flow. VOC and dissolved gas concentrations are highest in two large waste trenches located directly upgradient from the monitoring wells. Along the monitoring transect there is a decrease in solvent concentrations with distance from the trench, with TCE disappearing approximately 10 m from the end of the waste trenches and 1,2-DCE disappearing 35 m away, just before the groundwater discharges from a seep. VC and ethylene are still present at the seep, with ethylene showing peak concentrations at this locale. These results are strong indicators that anaerobic reduction of the chlorinated organics is occurring. In addition, the presence of high concentrations of methane throughout the site is also an indication of anaerobic conditions. Since ethylene concentrations are 100 fold larger than the chlorinated organics, the extent of anaerobic reduction is extraordinary. Another interesting finding is that the concentration of chlorinated organics is slightly higher in the matrix relative to the fracture regime, whereas the concentration of ethylene is lower in the matrix relative to the fracture regime. These results suggest that the fracture regime is slightly more effective in the anaerobic reduction of the chlorinated organics. Temporal variability of TCE and its degradation products is slight, with a general increasing concentration trend of chlorinated organics and dissolved gases as the site hydraulic gradient increases (a response to increased storm events during the winter and spring months). This may imply that the intrinsic bioremediation scenario at the site is less effective at higher discharge rates. Bacterial population data collected from the site indicate various populations of methanotrophs, total heterotrophs, and some sulfate reducing bacteria. The methanogenic population was not determined. The presence of methane oxidizers (methanotrophs) suggests possible zones of oxygenated groundwater which is confirmed with on- site DO measurements. Thus it appears there are two mechanisms of biological removal of chlorinated organic compounds occurring at the site. One pathway involves anaerobic dechlorination of TCE to VC and ethylene, and the other pathway involves oxidation of TCE to ethane via methane-oxidizing bacteria. Since both ethane and VC are present as possible degradation products of TCE, it is probable that both mechanisms are operative. At present it is not clear whether these processes are operating mainly in the relatively unweathered bedrock, where most of the wells are located, or whether they are also active in the upper few meters of highly weathered shale.

Fractured Till Column Experiments

An initial laboratory investigation of entry of immiscible TCE into a large (0.5 m x 0.5 m) cylindrical sample of fractured till, and its subsequent dissolution and diffusion into the matrix has been completed and a manuscript based on this research has been submitted to a major journal, Water Resources Research. After hydraulic testing of the sample, which yielded a mean hydraulic fracture aperture of 5 to 6 μm, immiscible-phase trichloroethene (TCE) was introduced to the column by incrementally increasing the head until entry occurred, which was followed shortly afterwards by discharge of TCE out of the bottom of the column. The entry-pressure corresponded to a calculated fracture aperture of 17 μm, which although larger than the hydraulically-determined value is still consistent, because it represents the aperture of the largest fractured, rather than an “averaged” value. The sample was allowed to sit for approximately three weeks and then was dismantled and the distribution of immiscible phase TCE in the fractures was determined by mapping of the dyed-TCE. Distribution of the dissolved phase TCE was determined using a miniature core sampling technique and subsequent extraction of dissolved TCE from the cores. After less than 1 month, there was very little TCE remaining in the fractures. Concentration measurements from the miniature

core samples showed that most of the mass of TCE had dissolved and diffused in the matrix where it formed a “halo” around the fractures. This rapid disappearance has several major implications for detection and clean-up of DNAPLs in fractured clays: first, the absence of immiscible DNAPL in monitoring wells or cores samples does not necessarily imply that the well or borehole has missed the DNAPL source zone; and second, remediation strategies aimed at removing the immiscible phase DNAPL are likely to be ineffective if there has been sufficient time since the initial spill for a significant portion of the DNAPL mass to diffuse into the matrix. Once in the matrix the dissolved DNAPL can still diffuse back into the fractures, but its removal will be largely diffusion-controlled.

Planned Activities

Weathered and Fractured Shale Column Experiments - two series of column experiments are in the preparation stage. The first will be to determine whether TCE residuals in fractures are rapidly depleted by dissolution and diffusion, as was observed in the experiments in fractured till. The second experiment will involve a simulated TCE spill in an undisturbed column of fractured and weathered shale, followed by flushing of the column with clean groundwater for a period of approximately one year to simulate natural flushing or remediation using pump and treat. The effluent will be monitored for TCE and degradation products and a mass balance will be carried out. Related to this, microcosm studies of TCE degradation and sorption will be carried out using the weathered soil to further study factors influencing the fate of the spilled TCE.

Natural Attenuation Field Site - This year we are planning to further characterize the plume and conduct a survey of bacterial populations in the groundwater using 16s rDNA analysis. The objective is to link specific bacterial populations with anaerobic dechlorination of TCE and its daughter products.

Till Columns - A second fractured till column is being set up for carrying out a multi-component DNAPL injection, to examine the influence of mixtures on entry-pressure and dissolution.

Other Access To Information

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In-Situ Characterization of Dense Non-Aqueous Phase Liquids Using Partitioning Tracers

Gary A. Pope, University of Texas at Austin

Research Objective

Major advances have been made during the past year in our research on interwell partitioning tracers tests (PITTs). These advances include: (1) progress on the inverse problem of how to estimate the three-dimensional distribution of NAPL in aquifers from the tracer data, (2) the first ever partitioning tracer experiments in dual porosity media, (3) the first modeling of partitioning tracers in dual porosity media, (4) experiments with complex NAPLs such as coal tar, (5) the development of an accurate and simple method to predict partition coefficients using the equivalent alkane carbon number approach, (6) partitioning tracer experiments in large model aquifers with permeability layers, (7) the first ever analysis of partitioning tracer data to estimate the change in composition of a NAPL before and after remediation, (8) the first ever analysis of partitioning tracer data after a field demonstration of surfactant foam to remediate NAPL, and (9) experiments at elevated temperatures.

Research Progress and Implications

Inversion of Tracer Data: We have developed a new analytic approach that has several advantages over existing approaches for inversion of tracer data. First, the technique utilizes an extremely efficient three-dimensional multiphase streamline simulator as a forward model. Second, the parameter sensitivities are formulated in terms of one-dimensional integrals of analytic functions along the streamlines. Thus, the computation of sensitivities for all model parameters requires only a single simulation run to construct the velocity field and generate the streamlines. The inversion of tracer data is then performed using a two-step iterative linearization that involves first 'lining-up' the breakthrough times at the producing wells and then matching the production history. Our approach follows from an analogy between streamlines and ray tracing in seismology. The inverse method is analogous to seismic waveform inversion and thus, allows us to utilize efficient methods from geophysical imaging. The new approach has been applied for estimating permeability distribution based on conservative tracer tests (D.W. Vasco and A. Datta-Gupta: "Asymptotic Solutions for Solute Transport: A Formalism for Tracer Tomography," Submitted to Water Resources Research, December 1997), and is currently being extended for analysis of partitioning tracer data.

In estimation of spatially distributed parameters such as permeability and DNAPL saturation, it has been recognized for a long time that data is never abundant enough to constraint the parameters uniquely. The new approach taken in this research is to recognize this fact from the beginning and to solve for an ensemble of solutions, each equally valid. The nonuniqueness issue is attacked from different perspectives. First, Genetic Algorithms (GAs), an efficient optimization search method, are used. GAs span the whole search space, act as a directed Monte-Carlo search and produces the initial set of valid solutions. Each solution is then refined using a classical gradient-based method. Second, the solutions are forced to be smooth in some sense by adding a penalty term to the objective function. Solutions showing unnatural variations of parameter values are thus penalized. Third, a cluster analysis is used to group together similar solutions. Characterization of the uncertainty of the solution, often overlooked, is treated fully through two approaches. They both involve the computation of the sensitivity matrix but extract different information from it. This approach is currently being tested on both realistic synthetic examples and field data from the saturated PITTs at Hill AFB and the unsaturated PITTs at Kirtland AFB.

Dual porosity media: The first ever partitioning tracer experiments were completed in dual-porosity rock. These studies are needed to understand the behavior of partitioning tracers in

such media, to compare with flow and transport models, to select the best tracers and operating conditions, and ultimately to determine the viability and applicability of partitioning tracer technology for characterizing nonaqueous phase liquid contamination in dual-porosity aquifers. The first experiment was done in a Berea sandstone with a single fracture with and without NAPL in the fracture. Figure 1 shows the separation of the nonpartitioning (IPA) and partitioning (n-heptanol) tracer response curves for one of the experiments with residual NAPL (decane) in the fracture. The results of these experiments clearly show the combined impacts of partitioning to the NAPL, fracture transport and matrix diffusion. To the best of our knowledge, no such experiments have been reported in the literature, so the experimental methodology, partitioning tracer technology and interpretation approach are all entirely new and must continue to be developed. A variety of other tracers with different diffusion coefficients and partition coefficients have been tested to start this process. An analytical model was used to interpret these partitioning tracer single-fracture studies. The model shows very good agreement with the laboratory results. The agreement indicates that the physical processes assumed in the model are similar to the actual processes occurring in the laboratory experiments. The understanding of these processes that we have gained is essential to continued development of partitioning tracer technology as applied to fractured aquifers. The first ever field scale modeling is under way using UTCHEM, a simulator which includes the necessary features for modeling both tracer partitioning and dual-porosity tracer transport. These simulations are essential for our understanding of the relative importance of various parameters and characteristics for partitioning tracer test design in fractured media. Inspectional analysis has been used to determine the appropriate nondimensional scaling groups to aid in the understanding and generalization of our studies with fractured media.

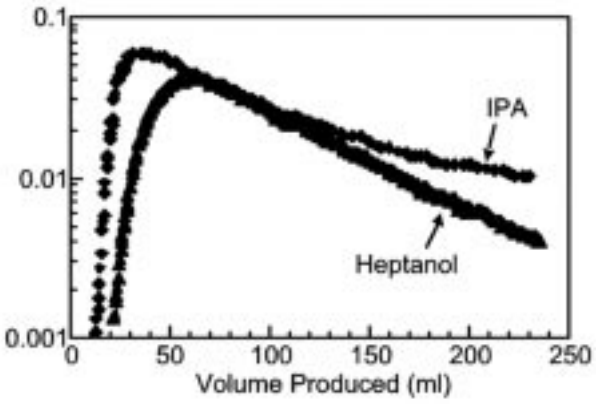

Figure 1: Dual-porosity experiment showing nonpartitioning and partitioning tracers

Compositional analysis: Two vadose zone partitioning interwell tracer tests were completed at Kirtland Air Force Base to evaluate a radio frequency enhanced soil vapor extraction remediation technology. The remediation effort was a project of the Advanced Applied Technology Demonstration Facility. This effort was the first attempt to estimate the change in the composition of the NAPL after remediation. The Peng-Robinson equation-of-state was used to model the thermodynamic interaction between the hydrocarbons and the partitioning tracers. From this interaction, the compositional effects were determined. The results are unique in that they give not only the volume of NAPL removed, but also the change in composition due to the remedial action. This work is relevant to the many field sites where the NAPL consists of a complex chemical mixture and where the remediation process causes large changes in its composition.

Complex NAPLs: Alcohol tracer partition coefficients for coal tar have been measured and are compared to similar values for several different NAPLs in Figure 2. Coal tar is a multicomponent dense, nonaqueous phase liquid (DNAPL) primarily composed of polycyclic aromatic hydrocarbons. Despite the great complexity of coal tar, the results in Figure 2 show that the partition coefficients

can be predicted using the equivalent alkane carbon number approach just as well as for simple NAPLs such as trichloroethylene and decane. We have also investigated other very complex NAPLs such as a fuel oil with very high viscosity and in all cases we have found that the equivalent alkane carbon number approach is useful for correlating the tracer partition coefficients.

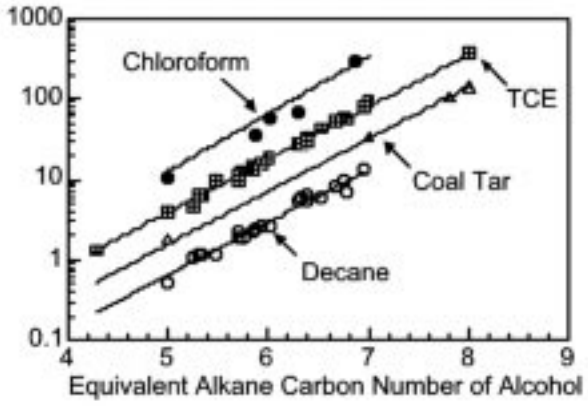

Figure 2. Comparison of predicted and measured partition coefficients of various alcohol tracers with various NAPLs.

Planned Activities

Not Provided

Development of Radon-222 as a Natural Tracer for Monitoring the Remediation of NAPL Contamination in the Subsurface

Lewis Semprini, Oregon State University

Jonathan Istok, Oregon State University

Research Objective

The objective of this research is to develop a unique method of using naturally occurring radon-222 as a tracer for locating and quantitatively describing the presence of subsurface NAPL contamination. The research will evaluate using radon as an inexpensive, yet highly accurate, means of detecting NAPL contamination and assessing the effectiveness of NAPL remediation. Laboratory, field, and modeling studies are being performed to evaluate this technique, and to develop methods for its successful implementation in practice.

Research Progress and Implications

This report summarizes work that has been accomplished after 1-year of a 3-year project. The research to date has included radon tracer tests in physical aquifer models (PAMs) and field studies at Site 300 of the Lawrence Livermore National Laboratory, CA, and Site 100D at Hanford DOE

Facility, WA. The PAM tests have evaluated the ability of radon as a tracer to monitor the remediation of TCE NAPL contamination using surfactant treatment, and oxidation with permanganate. The surfactant tests were performed in collaboration with Dr. Jack Istok and Dr. Jennifer Field and their EMSP project "In-situ, Field-Scale Evaluation of Surfactant Enhanced DNAPL Recovery Using a Single-Well-Push-Pull Test." This collaboration enabled the EMSP radon project to make rapid progress. The PAM surfactant tests were performed in a radial flow geometry to simulate the push-pull-method that is being developed for surfactant field tests. The radon tests were easily incorporated into these experiments, since they simply rely on measuring the natural radon present in the subsurface fluids. Two types of radon tests were performed: 1) static tests where radon was permitted to build-up to steady-state concentrations in the pore fluids and the groundwater concentrations were monitored, and 2) dynamic tests were the radon response during push-pull surfactant tests was measured. Both methods were found to be useful in determining how NAPL remediation was progressing.

Methods for conducting the surfactant test in the PAMs are described in the Progress Report of Istok and Field. The PAMs were packed with subsurface solids from Site 300, which emanated enough radon for its use as a natural tracer. Radon concentrations in 5 ml groundwater samples from the PAM were accurately measured using a low background Liquid Scintillation Method with Alpha-Beta-Discrimination Counting. Studies were performed with no NAPL present and with the addition of 5% TCE saturation to a portion of the PAM. Radon concentrations under static (no flow conditions) were a factor of two lower in the region that contained NAPL. The reduction in radon concentration, however, was not as low is predicted by partitioning theory. These results were consistent with TCE measurements and indicate that the TCE contamination was not uniformly distributed in the PAM. Results of dynamic tests showed radon transport being retarded due to the partitioning into the NAPL TCE, consistent with transport theory. Both static and dynamic radon tests were performed during the course of the push-pull surfactant experiments. The remediation with DPDS surfactant resulted in little change in the radon concentration distribution in the PAM, indicating minor amounts of NAPL TCE were removed. This result is consistent with direct TCE mass balances that were performed.

PAM tests were also performed of TCE NAPL remediation using permanganate oxidation. Experiments were conducted using a push-pull test methodology for the addition of the permanganate, similar to that used for the surfactant studies. Low and high concentrations of permanganate were injected during the course of the study. Static radon tests showed radon concentrations, that were initially reduced in the NAPL contaminated region of the PAM, increasing with permanganate additions. The most dramatic increases occurred near the end of the PAM where the permanganate was injected. The results agree with chloride mass balances that indicated oxidation of 35% of the inplace TCE. Dynamic push-pull tests, also show radon concentration responses changing during the course of the remediation. Water lacking radon was injecting during the push phase of the push-pull tests. During the pull-back phase, radon concentrations increased more rapidly as NAPL remediation progressed, consistent with transport theory. The results from the surfactant and the permanganate PAM studies illustrate the potential for using radon as a natural tracer to monitoring the progress of NAPL remediation in the field.

Field studies at the LLNL Site 300 included three preliminary radon tracer push-pull-well tests at the site. Preliminary groundwater radon surveys conducted prior to the start of the EMSP project showed depressed radon concentrations in region of the aquifer where NAPL contamination is expected. Tests were performed in wells containing low, intermediate, and high radon concentrations by injecting radon free water into the wells along with a bromide tracer. Consistent with transport theory, the radon concentrations increased most rapidly in the well with high radon concentration groundwater, and remained essentially constant in the well with low radon concentration groundwater. The results indicate the presence of NAPL in the region with low radon concentrations. The results illustrate how the radon method can be successfully employed with other push-pull tests for remediation that are being developed.

Studies at the Hanford Site were performed as part of test using partitioning gas tracers, to determine if trapped gas is present in the aquifer at Site 100D. These tests provided an opportunity to study a radon partitioning process that is similar to that which occurs with NAPLs. Two tests

were performed: 1) a push-pull-single well test, and 2) a radial injection transport test with sampling at a multi-level monitoring well. Radon free groundwater was injected in both tests. Again the radon method was easily incorporated into these tests and required only the monitoring of radon concentrations and no addition of tracer. The radon response indicated the presence of trapped gas in the aquifer, consistent with results obtained with partitioning tracers that had to be carefully added, such as SF6.

Planned Activities

Radon studies will be continued using the PAMs for NAPL remediation using push-pull methods. A new set of surfactant studies will be performed using Aerosol MA, which promises to be a more effective surfactant for TCE NAPL remediation. Radon tests will also be continued in PAM remediation experiments via permanganate oxidation of TCE. We will also initiate studies in a 2-D horizontal physical model that is packed with aquifer solids from the Hanford Site. The model is representative of aquifer conditions where regional flow is induced. Distributed TCE NAPL zones will be created in the 2-D model, and the groundwater radon concentration distribution will be determined before and after TCE is injected, and after TCE is remediated using permanganate and/or Aerosol MA. Push-pull tests will be performed within the 2-D model to simulate field scale tests.

We also plan to conduct experiments with Dr. Mart Oostrom at the PNL Laboratory at Hanford. Dr. Oostrom has a two dimensional vertical model with a Dual Energy Gamma System for measuring TCE and water saturations, permitting direct comparisons with the radon method for estimating TCE saturations. A radon survey is also planned for Savannah River, in collaboration with Joseph Rossabi, Westinghouse.

Other Access To Information

Semprini, L.M. Cantaloub, S. Gottipati, O. Hopkins, and J. Istok. Radon-222 as a Natural Tracer for Quantifying and Monitoring NAPL Remediation. Proceedings: First International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, May 18-21, 1998, Monterey, CA (In Press).

Surface Nuclear Magnetic Resonance Imaging of Water Content Distribution in the Subsurface

Jan M.H. Hendricks, New Mexico Institute of Mining & Technology

Research Objective

The objective of the project is to evaluate Surface Nuclear Magnetic Resonance Imaging (NMRI) for determining water content distribution in the subsurface. In NMRI the interaction of the magnetic moment of hydrogen (protons) nuclei with external applied electromagnetic (EM) fields is measured. In surface NMRI the Earth's magnetic field causes alignment of the spinning protons. An alternating EM field is generated by a loop of wire laid on the Earth surface. The alternating current driven through the loop at the Lamor frequency of protons in liquid water. The component of the EM field perpendicular to the Earth's field causes a precession of protons from thier equilibrium position. Water content distribution in the subsurface is derived from measurements on the EM field caused by the return of the precessing protons to equilibrium after the current in the transmitter loop is terminated.

The scientific goals of the R & D are:

- to verify and validate the theoretical concepts and experimental results of Russian scientists , who first introduced this method.
- to evaluate the range of applications and limitations of this technology for practical field measurements.

NMRI has the potential of providing a remote, direct, unique method for subsurface water measurements. All present methods are either intrusive or indirect (e.g. electrical resitivity measurements).

Research Progress and Implications

In the past year progress has been made along two separate paths. These are:

1) Field Measurements. Surface NMRI equipment manufactured by IRIS Instruments of France was tested over a number of sites with good hydrogeologic control. The results of these measurements can be summarized as follows:

   - The NMRI measurement directly and uniquely determines water distribution in coarse grained aquifers; geologic formation from which water can be readily withdrawn.
   - Water content can not be determined by this technique in fine grained sediments.
   - The signal to be measured is very small and EM interference's from power lines makes NMRI a difficult measurement in an urban setting.
   - The presence of minerals with a high magnetic susceptibility interfere with reliable measurements.

2) Theoretical Computations. The inversion of the experimental measurements requires the computation of the EM field within the Earth. We have extended these computations with the design of fast algorithms for computing the EM field for Earth stratified in electrical resitivity.

Planned Activities

We will continue to expand our field measurements over controlled hydrogeologic settings, so that the range of applications and limitations can be clearly understood.

Manipulating Subsurface Colloids to Enhance Cleanups of DOE Waste Sites

Philip M. Gschwend, Massachusetts Institute of Technology

Research Objective

This project seeks to increase the effectiveness of pump and treat systems for removal of pollutants from sandy aquifers. Pollutants which sorb strongly to aquifer solids are not efficiently remediated using pump and treat technologies. However, if the sorbents most active in immobilizing pollutants (e.g., clays, humics, and iron oxides) were dispersed into colloidal size particles (colloid mobilization), these colloids and their associated pollutants might be pumped from aquifers. At a chromium contaminated sandy aquifer, this project seeks to: (1) understand the forces which stabilize colloidal

particles in the aquifer, (2) devise solutions which will disrupt these colloid stabilizing forces, and (3) demonstrate the effectiveness of colloid mobilization as a remediation technique for removing sorbed chromium from the aquifer.

Research Progress and Implications

This progress report summarizes work completed after 1 1/2 years of a three-year project. Our efforts have focused on remediation of a chromium contaminated aquifer located on the property of National Chromium in northeastern Connecticut. Our work to date may be divided into three areas: (1) site characterization; (2) identification of colloid binding forces and development of an effective colloid dispersion treatment; and (3) field testing of the aquifer remediation strategy.

(1) Site Characterization

National Chromium is a chromium plating company which has been in operation since approximately 1940. The sandy aquifer underlying the plant is contaminated with chromium due to past manufacturing practices. Ninety nine percent of the chromium in the aquifer is sorbed to aquifer solids (Nikolaidis et al., 1994).

In June and September 1997, soil cores and water samples were collected from the site to characterize the mineralogy and determine the extent of chromium contamination at the location of future remediation tests. These cores also provided material for laboratory experiments elucidating mechanisms of colloid attachment and dispersal. We also performed pumping and slug tests to determine the aquifer's hydraulic conductivity.

The aquifer contains fine to silty sands with, in some areas, gravel and small stones. Aquifer material derives from both glacial and river deposits and appears to vary in texture and chromium content depending on its origin. Hydraulic conductivities are on the order of 10^{-5} to 10^{-6} cm/sec. In the vicinity of the cores collected in 1997, groundwater is oxic with pH values around 4.1. Dissolved chromium levels (presumably as $HCrO_4^-$) range from 38 to 51 mg/L. Chromium levels vary both horizontally and vertically (84 to 590 μg Cr/g dry sediment). After aggregates were dispersed by sonication, size fractionation of one sample revealed 90 % of the chromium and 74% of the iron to be in the less than 74 μm fraction. Mineral analysis indicated the presence of quartz , probably mica, and possibly chlorite, vermiculite, and feldspar in aquifer sediments. No crystalline iron minerals were observed suggesting that the 2.5 to 0.94 % iron found in the aquifer is contained in clay minerals and amorphous oxides.

(2) Identification of Colloid Binding Forces and an Effective Colloid Dispersion Treatment

Batch tests were performed with aquifer materials and solutions designed to mobilize colloids stabilized by different types of forces (e.g., electrostatic, covalent bonds, cementatious phases) (Swartz and Gschwend, 1998). A review of the literature and previous work performed at this site indicated that iron oxides should play a major role in binding chromium to aquifer solids; therefore, batch tests were also designed to specifically attack amorphous oxide phases. Initial tests were performed on aquifer materials with the highest chromium contents. Batch experiments were designed to quantify dissolved chromium and chromium associated with particles 7 μm or less in diameter. Solutions used in batch experiments include water, and aqueous solutions of phosphate, ascorbate, and citrate at different pH values as well as combinations of these compounds.

Citrate solutions (1.0 mM) at pH values of 5.5 or greater were found to remove roughly half the sediment chromium. Citrate solutions appear to mobilize a fine sediment fraction, probably consisting of amorphous iron oxides and clay minerals, which is not strongly bound to sand grains. Treatment effectiveness is highly pH dependent which suggests that changing particle surface charge is crucial to dispersing this fine fraction.

(3) Field Testing of the Aquifer Remediation Strategy

Single well injection-withdrawal experiments will be used to determine the effect of colloid mobilization solutions on aquifer materials in-situ. An initial injection-withdrawal test using a bromide

tracer added to groundwater has been performed to check the performance of the pumping and packer system. This initial test was also designed to determine the increase in aquifer turbidity resulting solely from the injection-withdrawal procedure.

References

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C.H. Swartz and P.M. Gschwend. (1998) Mechanisms controlling release of colloids in groundwater in a southeastern coastal plain aquifer sand. Environmental Science and Technology, in press.

Planned Activities

Further batch experiments will be performed to characterize the forces which stabilize colloids in the aquifer and optimize colloid mobilization solutions. Single well injection-withdrawal experiments will be used to determine the response of the aquifer material to solutions designed to mobilize colloids. Additional field experiments involving examination of aquifer material exposed for several days to colloid mobilizing solutions in-situ may also be performed.

Colloid Transport and Retention in Fractured Deposits

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Larry D. McKay, University of Tennessee
Liyuan Liang, University of Wales, Cardiff
Motomu Ibaraki, Ohio State University
Paul Reimus, Los Alamos National Laboratory

Research Objective

The goal of the DOE project is to identify the chemical and physical factors that control the transport of colloids in fractured formations, and develop a generalized capability to predict colloid attachment and detachment based on hydraulic factors (head, flow rate), physical structure (fracture aperture), and chemical properties (surface properties of colloids and fracture surfaces). The research approach targets multiple scales, including: (a) a theoretical description of colloid dynamics in fractures that extend concepts used for porous media to fracture geometry, with predictions experimentally tested in simplified laboratory “fractures”; (b) colloid transport experiments in intact geological columns, which provide natural complexity, but mass balance data and experimental control over flow, colloid size, ionic strength and composition; (c) field-scale transport experiments using colloidal tracers to examine realistic scales of fracture connectivity; and (d) modeling of colloid transport in complex fracture networks that include fractures with varying flow rates and permitting colloid diffusion into microfractures. Understanding the processes that control colloid behavior will increase confidence with which colloid-facilitated contaminant transport can be predicted and assessed at contaminated DOE sites. An added benefit is the expectation that this work will yield novel techniques to either immobilize colloid-bound contaminants in-situ, or mobilize colloids for enhancing remedial techniques such as pump-and-treat and bioremediation.

Research Progress and Implications

This report summarizes work after 20 months of a 3-year project. Progress in the four project elements (tasks) is summarized below:

A) Fundamental Description of Particle Transport in Fractures

This modeling effort represents the first theoretical description of the electrostatic and physical processes controlling colloid interactions with surfaces within a fracture geometry. Using a particle tracking method, an algorithm has been developed to describe the colloid dynamics in fractures, including consideration of particle diffusion, sedimentation under gravity field, and probability of particles sticking to fracture walls under infinite plane geometry. We found that a steady state solution is attained. The particle diffusion and collection by walls are most significant, compared to gravitational sedimentation. We have also derived an analytical solution for large Peclet numbers under steady state (expressed in terms of parabolic cylinder functions). We next plan to check on the agreement between this solution and the steady state solution given by the particle-tracking model. An experimental system of 1-D parallel-plate "artificial fractures" with SiO_2-coated "fracture walls" is being used to test and validate the model predictions. The results of this task will advance fundamental descriptions of colloid migration in fractures, and will also provide a theoretical foundation for parameterizing filtration coefficients that are used in the geochemical transport model of colloid migration in fracture networks (below).

B) Colloid Transport in Intact Geological Columns

Two series of colloid tracer laboratory experiments have been completed using undisturbed column samples of weathered fractured saprolite. The first series of experiments investigated the influence of particle diameter on colloid transport in undisturbed columns of the fractured shale saprolite. The experiments showed that there was an optimum size of 0.5 to 1.0 mm for transport of the latex microsphere tracers. Loss of the smaller-than-optimum particles was attributed the more rapid diffusion of the smaller particles, leading to more collisions with, and retention by, the fracture walls. Dismantling of the soil column and mapping of distribution of the microspheres clearly showed evidence of size segregation of particles within the fractures, with the smaller microspheres penetrating into the fine-grained matrix between fractures.

A second series of experiments to examine the influence of ionic strength and cation valence in the carrier solution has also been completed. In these experiments 4 different sizes of latex microspheres (0.1-2.1mm) were passed through a saprolite column in carrier solutions containing different ionic strengths of monovalent (Na^+) and divalent (Ca^{2+}) cations. As expected, for both the monovalent and divalent cases, colloid retention increased as ionic strength increased. As well, retention was greater for the experiments with the divalent carrier solution, relative to experiments with the monovalent carrier solution. Further evaluation is underway to determine deposition rates and collector efficiencies for the different sizes of colloids.

This project is also being assisted through a research transfer element of DOE/OBER's Subsurface Science Program (SSP). A SSP project (G. Moline, PI) is developing improved techniques to characterize fracture networks, using, for example, x-ray tomography to visualize and analyze the statistical distribution of fracture networks. We hope to utilize these techniques in place of the expensive, time-consuming, and destructive core dissection so that transport models can accurately represent the column either as discrete fracture networks with representative characteristics, or in a Monte-Carlo fashion using actual statistical distributions for the characteristics.

C) Field-Scale Colloid Tracer Migration

Two series of field tracer experiments were completed. The first experiment at a radionuclide-contaminated DOE site was conducted in the same saprolite formation from which the intact columns were excavated. Groundwater at the site contained near-saturated levels of $CaCO_3$. Two sizes of colloids (0.8- and 2.0-μm) and a nonreactive tracer were injected. Results demonstrated that colloid

transport was very limited (consistent with the effects of high Ca levels observed in the column studies). At a monitoring location only 1-m from the injection well, recovery of colloids was an order of magnitude below that of the nonreactive tracer (relative to the source concentrations of each tracer), and recovery decreased another order of magnitude at a distance of 3-m. However, the size discrimination observed in the column experiments was not observed in the field experiments, suggesting that interconnections between fractures occurring at larger spatial scales may permit greater transport of larger colloids than predicted from the column-scale studies. Colloids retained by the formation could be mobilized by experimental manipulation of ionic strength. When distilled water was introduced into the injection well three weeks after the colloid injection ceased, the concentration of colloids in the downgradient monitoring well increased by two order of magnitude within a few days.

Hypotheses concerning the effects of water chemistry and fracture network characteristics were tested at the second experimental site. The ionic strength of the groundwater at the second site was less than half that at the first site; furthermore, colloids were injected into wells screened in two contrasting lithologies: a highly weathered saprolite similar to the intact column (characterized by a dense network of small fractures), and an underlying rubbly, weathered bedrock (characterized by larger, more widely-spaced fractures). Four sizes of colloid were injected into each lithology, with each colloid uniquely identified by a fluorescent dye. Preliminary data suggests: (1) there is considerably greater mobility of colloids at the second site compared to the first site, consistent with the lower ionic strength, and (2) that there are very significant differences in the rate and extent of colloid transport in the two lithologies, with much greater retention of small colloids in the densely-fractured upper zone. These results are consistent with the ionic strength studies at the column scale (above), and with predictions from the fracture network model (below).

D) Modeling Colloid Transport in Complex Fracture Networks

The fracture network modeling has focused on determining the relative importance of the processes controlling the migration of colloids through fractured media, as well as further development of the FRACLD code to include the additional processes of remobilization of colloids and their diffusion into the matrix. Some of the processes considered for the sensitivity analysis were the filtration coefficient (reflecting the extent of colloid retention by the fracture walls), fracture network density, fracture lateral network extent, and dispersivity. Simulation results show that the size and, especially the density of these fracture networks were the single most important attribute determining the overall migration and eventual breakthrough of the colloidal particles. Increasing the density of fractures delays the arrival time for colloids. For example, a ten-fold increase in the number of fractures results in a five-fold increase in the time required for the colloid concentration to reach 80% of the source concentration. The importance of fracture density seen in these model simulations is consistent with the results of the field study in the contrasting lithologies (above). The results are also consistent with results from the collaborating SSP project, which examined solute and colloid transport in intact column experiments in which flow was oriented parallel-to-bedding or perpendicular-to-bedding. Less recovery of both tracers was observed for transport parallel-to-bedding, which is characterized by a high density of narrow fractures, than for transport perpendicular-to-bedding, where transport is through fewer, wider fractures, and a greater number of horizontal connecting fractures.

Significance

This work has yielded new insights into colloid transport and it's importance to contaminant mobility at DOE sites by quantifying the importance of both physical factors (particle diameter, flow velocity, and fracture density) and chemical factors (ionic strength, cation valence, and likely pH of the carrier solution) on the potential for colloid transport. The demonstrated effects of ionic composition in the column studies, and the observed release of colloids following ionic strength adjustment in the field experiment highlights the possibility that colloid transport behavior may change seasonally or over shorter time-frames due to variations in influx of meteoric water. For example, during seasonally wet periods there are typically large increases in flow rate and some decrease in ionic

strength, which could result in mobilization and rapid transport of colloids during these periods. As a result, migration of colloidal contaminants might be highly intermittent, and this should be considered in designing monitoring strategies.

Planned Activities

The analytical model of colloid interactions in fractures will be compared with the particle-tracking model within the next few months. Single-fracture transport experiments to test the model predictions will be conducted this Summer and Fall. Another series of intact column experiments will be conducted over the next year to examine the effect of colloid surface charge on transport. A series of field experiments are planned in the Winter of 1999 to examine colloid transport in fractured bedrock, and to examine the effect of colloid surface charge on field-scale migration of colloids. The modifications of the FRACLD model to include the processes of diffusion into fine pores and colloid remobilization will be completed within the next six months. These modifications will also greatly increase the computational efficiency of the model which will allow for larger, more extensive, and field-scale simulations. Computer simulations of the column experiments are now underway and will be completed in the next year. Simulations of the field-scale experiments will be examined in the final phases of the project. The increases in the computational efficiency are expected to make the model available to users without access to high-end work stations. Thus, by the end of the project, a simulation tool will be available to predict the field-scale transport of colloids, based on improved fundamental understanding and tested on column and field experiments that incorporated the key variables controlling colloid transport in subsurface systems.

Characterization of Contaminant Transport by Gravity, Capillarity and Barometric Pumping in Heterogeneous Vadose Regimes

Charles R. Carrigan, Lawrence Livermore National Laboratory

G. Bryant Hudson, Lawrence Livermore National Laboratory

Research Objective

The intent of this research program is to obtain an improved understanding of vadose zone transport processes and to develop field and modeling techniques required to characterize contaminant transport in the unsaturated zone at DOE sites. For surface spills and near-surface leaks of chemicals, the vadose zone may well become a long-term source of contamination for the underlying water table. Transport of contaminants can occur in both the liquid and gas phases of the unsaturated zone. This transport occurs naturally as a result of diffusion, buoyancy forces (gravity), capillarity and barometric pressure variations. In some cases transport can be enhanced by anisotropies present in hydrologic regimes. This is particularly true for gas-phase transport which may be subject to vertical pumping resulting from atmospheric pressure changes. For liquid-phase flows, heterogeneity may enhance the downward transport of contaminants to the water table depending on soil properties and the scale of the surface spill or near-surface leak. Characterization techniques based upon the dynamics of transport processes are likely to yield a better understanding of the potential for contaminant transport at a specific site than methods depending solely on hydrologic properties derived from a borehole. Such dynamic-characterization techniques can be useful for evaluating sites where

contamination presently exists as well as for providing an objective basis to evaluate the efficacy of proposed as well as implemented clean-up technologies. The real-time monitoring of processes that may occur during clean-up of tank waste and the mobility of contaminants beneath the Hanford storage tanks during sluicing operations is one example of how techniques developed in this effort can be applied to current remediation problems. In the future, such dynamic-characterization methods might also be used as part of the site-characterization process for determining suitable locations of new DOE facilities that have the potential of introducing contamination into the vadose zone.

Research Progress and Implications

This report summarizes work and accomplishments at the midpoint of our 3-year project. We have pursued the concept of a vadose-zone observatory (VZO) to provide the field laboratory necessary for carrying out the experiments required to achieve the goals of this research. Our approach has been: (1) to carry out plume release experiments at a VZO allowing the acquisition of several different kinds of raw data that, (2) are analyzed and evaluated with the aid of highly detailed, diagnostic numerical models. Because the soil properties of a single VZO are unlikely to cover the full range of conditions encountered at all DOE facilities, we anticipate studying at least two and possibly three sites spanning a wide range of hydrologic and geologic properties.

The key feature of the VZO constructed at Lawrence Livermore National Laboratory (LLNL) is the variety of plume-tracking techniques that can be used at a single location. Electric resistance tomography (ERT) uses vertical arrays of electrodes across the vadose zone that can monitor electrical resistance changes in the soil as a plume moves downward to the water table. These resistance changes can be used to provide “snapshots” of the progress of the plume. Additionally, monitoring wells have been completed at multiple levels in the vicinity of a central infiltration site. Sensors emplaced at different levels include electrically conducting gypsum blocks for detecting saturation changes, thermistors for monitoring temperature changes and pressure transducers for observing barometric changes at different levels in the vadose regime. The data from these sensors are providing important information about the state of the gas- and liquid-phase dynamics of the infiltration process. Similarly, access ports at different levels have been used to supply gas-phase samples while lysimeters will soon yield liquid-phase samples. Studies involving gas-phase tracers are being carried out concurrently at LLNL and at an Orange County Water District site in southern California. With this type of information, the time-dependent chemical signature of a plume that has been spiked with an array of dissolved noble-gas tracers is being studied. We are also beginning to correlate chemical signatures with those of the above-mentioned sensors that track the physical changes in the vadose zone.

From the VZO at the LLNL site and from 3-D diagnostic simulations of our first plume infiltration event, we are beginning to develop a better understanding of the implications of soil heterogeneity for unsaturated zone contaminant transport at DOE sites. Even though the LLNL VZO site might be considered to be hydrologically “tight” owing to the low permeability of the clays and silts that dominate the soil formations there, we find that saturation increases resulting from a near-surface “leak” reach the water table across the 20-meter-thick vadose zone in only tens of hours to days. This rapid transport at the site cannot be accurately simulated by layered models that derive their hydrologic properties from borehole-soil samples. Only simulations assuming a heterogeneous regime “threaded” by extremely high-permeability pathways can explain the rapid increase in saturation observed with ERT near the water table. Three-dimensional predictive models of a hypothetical tritiated water leak that are based on the above mentioned diagnostic models have now been run. The models suggest that the hypothetical tritium leak would be expected to reach the water table at significant concentrations within a few days of release. Because heterogeneity and “fast paths” are so important for understanding the transport of contaminants to the water table, one- and even two-dimensional models of layered soils are likely to be inadequate for evaluating vadose zone transport processes. It is likely that contaminant transport under the mixed-waste tanks at Hanford, for example, could be better understood with the aid of dynamic characterization experiments and diagnostic modeling similar to that carried out for the LLNL VZO site.

Planned Activities

As we enter the last half of our 3-year research program, we have initiated parallel efforts to continue field experimentation and carry out both diagnostic and predictive analyses of the field data using the LLNL developed NUFT flow and transport code. Massive amounts of barometric pressure data have been recorded at the surface and at more than 30 subsurface ports associated with the VZO. As another dynamic characterization experiment, this data will be evaluated as a means of estimating the bulk hydrologic properties of the site. New infiltration experiments at the LLNL VZO site have also been planned. They are intended to investigate the effect of the leak volume on transport to the water table. The transport of liquid-phase tracers will be studied with the help of new wells to the water table, borehole lysimeters and conservative chemical tracers such as KBr. Given recent interest in the transport of plutonium by colloids, we are investigating the addition to synthetic plumes of fluorescent microspheres permitting analog studies of colloidal transport.

Diagnostic & Predictive Modeling (1.5 yr) **********(3 yr)
VZO Field Experiments ********** (2.5 yr)
Orange Co./LLNL Site 300 Expts. **********
Dissemination of Results (Papers/Meetings) **********

Other Access To Information

Hudson, G.B., "Isotope Tracers for Tracking Groundwater Recharge." California Water Reuse Association, Artificial Water Recharge Workshop, Newport Beach, CA, April 5, 1997.

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Chaotic-Dynamical Conceptual Model to Describe Fluid Flow and Contaminant Transport in a Fractured Vadose Zone

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Research Objective

DOE faces the remediation of numerous contaminated sites, such as those at Hanford, INEEL, LLNL, and LBNL, where organic and/or radioactive wastes were intentionally or accidentally

released to the vadose zone from surface spills, underground tanks, cribs, shallow ponds, and deep wells. Migration of these contaminants through the vadose zone has lead to the contamination of or threatens to contaminate underlying groundwater. A key issue in choosing a corrective action plan to clean up contaminated sites is to determine the location, total mass, mobility and travel time to receptors for contaminants moving in the vadose zone. These problems are difficult to solve in a technically defensible and accurate manner because contaminants travel downward intermittently through narrow pathways driven by variations in environmental conditions. These preferential pathways can be difficult to find and predict.

The primary objective of this project is to determine if and when dynamical chaos theory can be used to investigate infiltration of fluid and contaminant transport in heterogeneous soils and fractured rocks. The objective of this project is being achieved through the following Activities

1) Evaluation of chaotic behavior of flow in laboratory and field experiments using methods from non-linear dynamics;
2) Evaluation of the impact these dynamics may have on contaminant transport through heterogeneous fractured rocks and soils, and how it can be used to guide remediation efforts;
3) Development of a conceptual model and mathematical and numerical algorithms for flow and transport, which incorporate both: (a) the spatial variability of heterogeneous porous and fractured media, and (b) the description of the temporal dynamics of flow and transport, which may be chaotic; and
4) Development of appropriate experimental field and laboratory techniques needed to detect diagnostic parameters for chaotic behavior of flow.

This approach is based on the assumption that spatial heterogeneity and flow phenomena are affected by non-linear dynamics, and in particular, chaotic processes. The scientific and practical value of this approach is that we can predict the range within which the parameters of flow and transport change with time in order to design and manage the remediation, even when we can not predict the behavior at any point or time.

Research Progress and Implications

This progress report summarizes work after 1.5 years of a 3-year project.

Ponded infiltration tests were conducted in Idaho at two fractured rock field sites: the Hell's Half Acre (the scale of 1 by 0.5 m) and the Box Canyon (the scale of 7 by 8 m) sites. Using monitoring of water movement at drip points, geophysical imaging, in-situ measurements of the moisture content, water flow rate, water pressure in the rock matrix and fractures, subsurface tracer distribution, and other critical parameters, the temporal and spatial evolution of unsaturated flow in fractured rock were characterized for the first time in fractured basalt. Several new technologies have been developed specifically for this project including piezoelectric probes, a leak detection system, a laser surveying system, and a 3D Electrical Resistivity Tomography system.

Laboratory experiments were conducted to evaluate the presence of chaotic behavior in water seepage through fracture models, which have shown the pervasiveness of highly localized and extremely non-uniform flow paths in the plane of the fracture. Using the time-trend of a pressure signal for unsaturated flow in fracture models, the magnitude of deterministic-chaotic and stochastic components in the data were analyzed. For this purpose, several parameters were determined such as Hurst exponent, Lyapunov exponent, capacity dimension, correlation dimension, information dimension, correlation time, and constructed two-dimensional and three-dimensional attractors in phase-space.

Numerical modeling of the Box Canyon ponded infiltration tests using the TOUGH2 code with an explicit, yet simplified, representation of the key geologic and hydrogeological features (a hierarchical pattern of column-bounding and column-normal fractures in fractured basalt) confirmed: (a) the presence of complex, irregular flow paths for liquid-phase tracer, as well as air trapping and escaping in the vadose zone, and (b) the temporal aspects of chaotic flow, identified in laboratory and field experiments, cannot be captured using conventional modeling approaches.

Theoretical studies have shown that as a fluid film flows vertically on a fracture surface, it is inherently unstable and may exhibit chaotic behavior, even for low Reynold's numbers. Film waviness

may enhance transfer of contaminants from rock to fluid by as much as five times carrying contaminated fluid down a fracture much faster than expected by classical flat film theory.

The scientific significance of the research rests in: (a) the unique non-linear dynamics analysis of data sets such as fracture and matrix flow rates, pressure, and tracer concentrations, and (b) the development of a new dynamical chaotic model for flow and transport in fractured media. The results of this project are expected to change the conventional approach of using traditional stochastic and/or deterministic methods to predict flow and transport in environmental systems. Because the non-linearity of environmental systems limits their predictability into the future, we aim to determine how far into the future it is realistic to predict the state of the environmental system, and what the bounds on the time of contaminant transport are, and how long we can expect clean-up to take. The significance of the research for the DOE will be in the form of technology developed for vadose zone monitoring and in improved vadose zone site characterization and predictability.

Planned Activities

Additional field and laboratory experiments will be conducted in 1998 to examine the fracture/matrix interactions. Analysis of existing data from DOE sites (INEEL, LBNL, LLNL, and other) will be provided in 1998-99. Reports and publications will be written and made available to the environmental community at large. The methodology developed will be recommended to DOE sites where monitoring and remediation of contaminants using vacuum extraction, air stripping, steam injection, barriers, etc. are problems.

Other Access To Information

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On the Inclusion of the Interfacial Area Between Phases in the Physical and Mathematical Description of Subsurface Multiphase Flow

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Research Objective

Improved capabilities for modeling multiphase flow in the subsurface requires that several aspects of the system which impact the flow and transport processes be more properly accounted for. A distinguishing feature of multiphase flow in comparison to single phase flow is the existence of interfaces between fluids. At the microscopic (pore) scale, these interfaces are known to influence system behavior by supporting non-zero stresses such that the pressures in adjacent phases are not

equal. In problems of interphase transport at the macroscopic (core) scale, knowledge of the total amount of interfacial area in the system provides a clue to the effectiveness of the communication between phases. Although interfacial processes are central to multiphase flow physics, their treatment in traditional porous-media theories has been implicit rather than explicit; and no attempts have been made to systematically account for the evolution of the interfacial area in dynamic systems or to include the dependence of constitutive functions, such as capillary pressure, on the interfacial area.

This project implements a three-pronged approach to assessing the importance of various features of multiphase flow to its description. The research contributes to the improved understanding and precise physical description of multiphase subsurface flow by combining: 1) theoretical derivation of equations, 2) lattice Boltzmann modeling of hydrodynamics to identify characteristics and parameters, and 3) solution of the field-scale equations using a discrete numerical method to assess the advantages and disadvantages of the complete theory. This approach includes both fundamental scientific inquiry and a path for inclusion of the scientific results obtained in a technical tool that will improve assessment capabilities for multiphase flow situations that have arisen due to the introduction of organic materials in the natural environment.

Research Progress and Implications

This report summarizes work after 1.5 years of a 3-year project. The simulation aspects of the work rely on the availability of a continuum model for multiphase flow that incorporates processes of interest. Such a model serves to identify the data that must be extracted from the lattice Boltzmann model and provides guidance for the development of a model of field scale equations appropriate for a system of interest. Because the equation development is a precursor to the other aspects of this study, and because of logistical issues in securing the funding for the national laboratory components of the work, most of the effort has been directed to equation development and quantitative assessment based on the lattice Boltzmann simulator.

The theoretical analysis is based on the premise that physical description of multiphase flow in porous media ideally should be based on conservation principles. In practice, however, Darcy's law is typically employed as the foundation of multiphase flow studies. Darcy's law is an empirical surrogate for momentum conservation based on data obtained from experimental study of one-dimensional single phase flow. In its original form, Darcy's law contained a single, constant coefficient that depended on the properties of the medium. Since 1856, Darcy's relation has been heuristically and progressively altered by allowing this coefficient to be a spatially dependent, non-linear function of fluid and solid phase properties, particularly of the quantities of these phases within the flow system. The shortcoming of this approach is that the governing flow equation is obtained by enhancing a simple empirical coefficient with complex functional dependences rather than by simplifying general conservation principles. As a result, some of the important physical phenomena may not be properly accounted for. Also, some assumptions intrinsic to the equations are overlooked, making accurate simulation more of an art than an entirely scientific exercise. A more general approach employs a mathematical procedure for deriving conservation principles at the length scale of interest, followed by imposition of thermodynamic constraints to restrict the generality of these expressions. This approach provides a framework in which the assumptions inherent in a hypothesized model of multiphase flow are clearly stated. Requirements for more comprehensive and physically complete models can then be specified.

The contributions to this area of research under the current project is in four areas. First, a manuscript [1] has been prepared which discusses the shortcomings of heuristic extensions of Darcy's observations to more general problems of single and multi-phase flow. This paper also argues for the importance of consistent and integrated theoretical, computational, and experimental work for progress in understanding multiphase flow. Second, the complete framework for the derivation of conservation equations for phases, interfaces, common lines, and common points has been presented [2]. Third, a comprehensive thermodynamic approach to macroscale system behavior has been implemented [3] which must also be supplemented by mechanical equilibrium constraints for the subscale geometric descriptors of the system [4].

Although not reported in the publications, additional work has been initiated to develop a reduced set of the balance equations for a simplified core-scale physical system. These will be used for the initial development of the continuum scale model and for the identification of constitutive parameters from the lattice model simulations. In light of the constitutive forms that arise in the analysis, several issues relating to the design of the lattice model simulations, as well as the extraction of sufficient and appropriate data from them, have been identified; and some success has been achieved in calculation of the needed information [5].

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Planned Activities

Over the next 1.5 years, activities are planned in all three areas of the research project. The theoretical study will incorporate chemical species transport into the full set of equations (6 mos.), extend the mechanical analysis to include four phase systems (1 yr.), and assess the ability of the theoretical approach to account for disjoining pressure in macroscale analysis (1.5 yr.). The lattice Boltzmann work will be re-implemented on current architecture for large scale high performance computing. (6 mos.). Additionally, a variable grid lattice method that has been developed will be tested. This will allow for more efficient simulation at the pore scale and enhanced ability to extract data (1 yr.). Based on lattice simulations, data analysis will be performed to obtain, as a primary constitutive function, the dependence of capillary pressure on interfacial areas as well as saturation. Dynamic relations among geometric parameters obtained from the theoretical analysis will be tested in the lattice Boltzmann framework (1.5 yr.). As improved equations and the data to support them are developed, the results will be tested in the numerical simulator of the equations (1.5 yr.).

Establishing a Quantitative Functional Relationship Between Capillary Pressure Saturation and Interfacial Area

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William G. Gray, University of Notre Dame

Research Objective

Through an integrated and focused research program that is comprised of theoretical, computational and experimental efforts this research effort is directed at: 1) improving on newly developed laboratory techniques to quantify and directly measure the functional relationship between phase interfacial area (a), saturation (S) and capillary pressure (Pc), 2) developing new computational

algorithms in conjunction with laboratory measurements to predict Pc, S and a, 3) testing existing theory and developing new theory to describe the relationship between Pc, S and a at the large scale, and 4) synthesizing the results of the experimental, computational and theoretical investigative efforts to develop a generic model based upon an intrinsic soil metric to describe the functional dependence of Pc, S and a.

The results of this research could be used to generate a site specific soil moisture characteristic surface. Ultimately the results of this research could serve as the foundation upon which the true health and safety risk of a site could be evaluated, the applicability of various remediation technologies examined, and the performance of implemented treatment strategies controlled.

Research Progress and Implications

This report summarizes work after 18 months of a 3-year project. We are working to integrate the theory, experiments, and numerical simulations into a coherent approach to study the role of interfacial areas in porous media flow physics. Our recent efforts have focused on quantifying the relationship between capillary pressure, saturation, and interfacial areas. The theory developed by Gray et al. (1998) indicates clearly that the traditional relationship between capillary pressure and saturation is incomplete, and interfacial area per unit volume must be added to the functional dependence. The theory does not, however, provide the form of that functional dependence; determination of this relationship must be done experimentally. To this end, both the network modelling and the PVI approach are being pursued.

The first results that investigated the relationship between Pc, Sw, and awn were reported by Reeves & Celia (1996). The results were based on a standard pressure-cell experimental setup, with capillary pressure imposed by controlling phase pressures along boundaries. A pore network with approximately 200 000 pore bodies was used, with saturation and interfacial area calculated for approximately 8000 discrete values of capillary pressure. While the relationship between Pc and awn, and between Sw and awn, are very complex, the relationship between Pc, Sw, and awn is remarkably smooth and well-behaved. The general shape of the Pc-Sw-awn surface is consistent across a number of different lattice realizations and sizes.

A number of additional results come from the theoretical developments. For example, as mentioned earlier, the theory suggests that the permeability coefficient should be a function of interfacial area. The computational network can again be used to examine the form of this proposed functional dependence. The work of Reeves (1997), presents a calculated relationship between relative permeability to the wetting phase, krw, saturation Sw, and fluid-fluid interfacial area awn. This initial result, which has not been extensively tested over a range of pore networks, indicates that the functional dependence of permeability on interfacial area is relatively weak.

Another conjecture that arises in the theoretical development is that hysteresis in the relationship between Pc and Sw arises because of the incomplete functional dependence, and that proper inclusion of areas will mitigate, or even eliminate, hysteresis. Reeves (1997), and Celia et al. (1998), have examined the question of hysteresis between the Pc-Sw-awn surfaces generated by both drainage scanning curves and imbibition scanning curves, and found that hysteresis does not disappear. Whether it is reduced in any significant way remains open to debate.

While these results, and others such as those reported in Reeves (1997), demonstrate how the network models can be used to test some of the theoretical results, the network models themselves remain relatively untested. Network models can be used to match measured capillary pressure - saturation and relative permeability - saturation relationships (see, for example, Rajaram et al., 1997). However, this does not mean that the interfacial area calculations are representative of actual porous media. Therefore the PVI experimental technique (Montemagno and Gray, 1995) is critical to both validation of the network models, and to provision of a “ground-truth” data set against which to compare the theory.

The overall objective of our joint work is to use innovative experimental techniques to test (and, we hope, validate) both the computational network models and the theoretical results. PVI will allow the relationship between Pc, Sw, and awn to be determined directly. If the network models can be validated using PVI results, then the models can be used to test a variety of additional

theoretical results with much more confidence. In support of this objective the performance and capability of the PVI experimental method has been significantly enhanced in the past 18 months. A stable system has been developed for conducting the long-term experiments (ca. 6 months) necessary for creating a Pc, Sw, and awn data set (Zang, 1998). Additionally, a new mathematical algorithm for calculating the interfacial surface areas of PVI data sets has been developed (Ma and Montemagno, 1998). This new technique eliminates the manual analysis of PVI data thereby drastically reducing the time required to analyze the multi-gigabyte data sets and ensuring repeatability.

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Planned Activities

During the 18 months remaining on the project we will: 1) extending the network models to include dynamics, so that the theoretical results regarding dynamic capillary pressure can be tested, 2) incorporate realistic geometries into network models, based on pore-space imaging produced by the PVI technique, 3) obtain real Pc, Sw, and awn surfaces and use this information to validate network models, and 4) use the validated network model to develop a methodology for predicting interfacial area based on the soil moisture characteristic curve and soil grain geometry.

Other Access To Information

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Least-Cost Groundwater Remediation Design Using Uncertain Hydrogeological Information

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Research Objective

The objective of the project is to formulate, test, and evaluate a new approach to the least-cost design of groundwater contamination containment and decontamination systems. The proposed methodology employs 'robust optimization', the outer-approximation method of non-linear programming, and groundwater flow and transport modeling to find the most cost-effective pump-and-treat design possible given the physical parameters describing the groundwater reservoir are known with uncertainty. The result is a methodology that will provide the least-cost groundwater remediation design possible given a specified set of design objectives and physical and sociological constraints.

Research Progress and Implications

As of the end of the first year of this 3-year project we have developed and tested the concept of 'robust optimization' within the framework of least-cost groundwater-contamination-containment design. The outer-approximation method has been employed in this context for the relatively simple linear-constraint case associated with the containment problem.

In an effort to enhance the efficiency and applicability of this methodology, a new strategy for selecting the various realizations arising out of the Monte-Carlo underpinnings of the 'robust-optimization' technique has been developed and tested. Based upon observations arising out of this work a yet more promising approach has been discovered. The theoretical foundation for this most recent approach has been, and continues to be, the primary focus of our research.

Planned Activities

Because of the importance of the realization-selection process to the overall success of our project, we intend to focus primarily on this issue until it is suitably resolved. Further theoretical development, analysis and testing of our new methodolgy is required. We anticipate this will take approximately six months.

Upon completion of this task we will turn our attention to incorporating and evaluating our new realization selection technique within the framework of least-cost design of groundwater contamination containment. We anticipate test results will be forthcoming within twelve months.

Upon successful completion of this work we will turn our attention to the more challenging task of robust least-cost groundwater decontamination design under uncertainty. The development, analysis and testing of our methodology within this context will constitute the bulk of the remainder of our research effort.

Permeameters for In-Situ Characterization of Unsaturated Heterogeneous Permeability

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Research Objective

Thick unsaturated zones underlie many Department of Energy (DOE) landfills, industrial areas, and waste storage sites in the western United States and are the primary pathway for contaminants to migrate into underlying aquifers. The spatial variability of unsaturated hydraulic properties in these heterogeneous geologic materials directly influences the movement of water and non-aqueous phase liquids (NAPL's). Poor characterization of heterogeneity may lead to ineffective remedial designs and increased risk, requiring subsequent additional remedial actions at increased cost and time. Remedial design can be improved using probabilistic risk-based decision analysis, which requires a large number of hydraulic property observations. Laboratory methods for estimating the unsaturated permeability are expensive, time-consuming, and may not yield results representative of heterogeneous field conditions. Simple and rapid field methods for estimating in-situ unsaturated permeability are appealing and potentially cost-effective.

The primary objective of our EMSP research is to design, develop, and test new permeameters for use in spatial variability studies. We have established a series of permeameter design criteria, including: 1) measurements should be relatively rapid, 2) the total cost per data point should be low, 3) results would accurately reflect the variation of unsaturated hydraulic properties between sampled locations, 4) the volume sampled (measurement support) would be small, and 5) useful range would be relevant to the range of soil moisture conditions encountered at DOE sites.

Research Progress and Implications

This report summarizes work after year two of a 3-year project. We report our activities to date related to development and testing of techniques for inverting permeameter data, development of numerical tools for data inversion, error evaluation for permeameter design, and permeameter component design.

Analytical Inversion Techniques: We evaluated, developed, and verified parameter estimation methods for inverting steady-state permeameter data, including a variety of boundary conditions and source geometries. Several analytical and quasi-analytical techniques for inverting steady-state permeameter data yield estimates of unsaturated hydraulic conductivity at specific tensions that are independent of parametric models. This represents an advantage over numerical estimation techniques, because numerical estimation yields parametric-model-specific parameter values. Because the time-scales required to reach steady state are large, however, steady-state permeameter methods are inconsistent with our first design criterion.

Numerical Simulations: Numerical simulations of permeameter performance are an integral part of our approach to permeameter design. We evaluated a variety of unsaturated flow codes, but found that they were computationally inefficient, did not preserve the required precision, did not implement necessary iterative schemes, or lacked other required options (e.g., types of source). Because modification of these codes was not practical, we developed and verified a flexible, axisymetric, 2-D, Richard's equation, saturated/unsaturated flow code based on the Galerkin formulation of weighted residuals for finite elements with Newton iteration to handle the non-linearity. This code will be extended for 3-D problems.

Error Evaluation: We are evaluating the effect of error on the uncertainty of estimated spatial statistics to improve permeameter designs. Four types of error affect hydraulic property estimates: 1) measurement errors within the device, 2) boundary condition and flow geometry errors, 3) improper

model specification (e.g., hydraulic properties are not consistent with the parametric model used in inversion), and 4) systematic errors in data inversion. In addition, estimated spatial statistics may be biased by measurement-support-scale heterogeneity.

We have evaluated the effect of small measurement errors on estimated spatial statistics determined from permeameter data. We analyzed the tension permeameter because it is frequently used for estimating spatial statistics of unsaturated hydraulic conductivity. We considered only pressure transducer measurement error within the tension permeameter device and neglected all other sources of errors, and used a Monte Carlo approach for the error analysis . Our preliminary results suggest that small amounts of measurement error can potentially lead to very large uncertainties in estimated spatial statistics, especially for correlation length. We suspect that including the other sources of error will further increase the uncertainty in estimated spatial statistics. If the uncertainty in estimated spatial statistics is high, it may not be possible to directly measure some unsaturated hydraulic properties for use in spatial analysis.

Effect of Measurement Scale Heterogeneity: We hypothesize that measurement-scale heterogeneity will introduce additional uncertainty in estimated spatial statistics for unsaturated hydraulic properties. As a result, we are developing adjoint sensitivity analysis techniques to quantify the impact of measurement scale heterogeneity on hydraulic parameters estimated with various permeameter designs. This approach yields a quantitative measure of the sensitivity of a measured effective property to the heterogeneities present within the measurement support. We have successfully applied this approach to the air permeameter, an instrument that measures saturated hydraulic conductivity in air dry sediments.

Independent Estimates of Scaling Variables: We believe that independent estimates of scaling variables, saturated hydraulic conductivity and the air entry value, may be subject to less error, therefore, providing better estimates of spatial statistics. Both of these variables can be estimated with a modification of the air mini-permeameter device. We are currently validating this approach.

Device Design: We have completed preliminary permeameter component designs. The basic permeameter design is modular consisting of a water-source package, a hybrid air mini-permeameter, and an instrument package. Development of each package is proceeding independently, allowing for flexibility in specific permeameter configuration.

Planned Activities

We believe that measurement error and bias, caused by systematic errors and measurement-scale heterogeneity, can substantially increase the uncertainty in estimated spatial statistics for unsaturated hydraulic properties. We will, therefore, continue to investigate the effects of these errors and biases with emphasis on minimizing their effect in final permeameter designs. We will specifically examine: boundary condition and flow geometry errors, the effects of improper model specification, data inversion error, and the influence of measurement-scale heterogeneity on effective property bias.

Based upon these results, we will continue to refine and finalize permeameter component designs. Prototype components will be constructed, and their performance verified in the laboratory before field testing. Our final activity will be a field test of the final permeameter design. A field test site has already been selected, and permeameter testing will be performed at a U.S. DOE EMSP project site (project: A Hybrid Hydrogeologic - Geophysical Inverse Technique for the Characterization, Monitoring, and Risk Assessment of Leachates in the Vadose Zone) in Socorro, New Mexico.

We plan to request a no-cost extension for the present project. Little work was accomplished in the first year due to difficulties implementing a subcontract, and because the senior PI was on sabbatical.

A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals

Scott Goode, University of South Carolina

S. Michael Angel, University of South Carolina

Research Objective

The long-term goal of this project is to develop a system to measure the elemental composition of unprepared samples using laser-induced breakdown spectroscopy, LIBS, with a fiber-optic probe.

Research Progress and Implications

Research Accomplishments (Year 2)

- Fabrication of Second LIBS Spectrometer (High Spectral Resolution Echelle Instrument)
- Preliminary Design for LIBS in Aqueous Solutions
- Use of Acoustic-Optical Tuned Filter for Spatial Resolution
- Measuring the Influence of the Matrix on LIBS Signals

Research Accomplishments (Year 1)

- First Demonstration of LIBS Imaging Using Fiber Optics
- Combined LIBS and Raman Spectral Imaging in a Single Probe
- Established a Collaboration with David Cremers at LANL
- Developed a Method to Improve Launch Efficiency of High-Power Laser Pulses into an Optical Fiber Without Catastrophic Damage
- Applied AOTF to Plasma Imaging to Characterize the Plasma both Spatially and Temporally
- Development work near completion for high-resolution LIBS spectrometer.

Planned Activities

- Development of methods that can be used to mesure LIBS signals from aqueous solutions will continue.6/98-6/99
- Studies in progress to measure mass ratios of vaporized materials via dissolution followed by ICP-MS 6/98-12/98
- Evaluate the role of materials factors, such as case=hardeining-on the laser volatilization process 6/98-6/99
- Continue the study of crater size and correlate with both LIBS signal and with mass of material vaporized. 6/98-6/99
- Measure the spatial and temporal dependence of signals and background as a function of the experimental parameters. 6/98-6/99
- Evaluate spatial discrimination, in place of time resolution, as a tool that can be used in concert with high resolution spectroscopy to acquire LIBS signals. 12/98-6/99
- Continue the development of analytical methods for applied chemical analysis. 6/98-6/99

Novel Ceramic-Polymer Composite Membranes for the Separation of Hazardous Liquid Waste

Yoram Cohen, University of California at Los Angeles

Research Objective

There is a growing need in the fields of pollution prevention, remediation, chemical processing and water treatment for new processes capable of selectively separating and concentrating a target species, often present in dilute solution. Although membrane systems have been touted as the most probable means to achieve difficult liquid-phase separations, at a reduced energy consumption level relative to conventional technologies (e.g., distillation, extraction), selective membranes with adequate structural integrity and longevity are lacking. In order to meet the above challenge the current project is focused on the development of a novel and robust class of ceramic-supported polymer (CSP) membranes for pollution prevention and remediation applications that require the separation of liquid organic-aqueous and organic-organic mixtures. The CSP membranes combine the unique structural properties of ceramic membrane supports with the chemical selectivity of terminally-anchored polymer phases. An important outcome of the project is a new technology for the "tailor design" of novel and robust membranes for in-processes separation for recovery and recycle, effluent treatment, and selective replacement of energy intensive separation processes (e.g., distillation) in a variety of industrial applications.

Research Progress and Implications

This report summarizes the work progress over the last 1.75 years of a 3 year project. The objectives of the project have been to develop a new class of ceramic-supported polymeric membranes that could be tailored-designed for a wide-range of applications in remediation and pollution prevention. To date, a new class of chemically-modified ceramic membranes was developed for the treatment of oil-in-water emulsions and for the pervaporation removal of volatile organics from aqueous systems. These new ceramic-supported polymer (CSP) membranes are fabricated by modifying the pore surface of a ceramic membrane support by a graft polymerization process (Chaimberg and Cohen, 1994). The graft polymerization process consists of activating the membrane surface with alkoxy vinyl silanes onto which vinyl monomers are added via free-radical graft polymerization resulting in a thin surface layer of terminally anchored polymer chains. Reaction conditions are selected based on knowledge of the graft polymerization kinetics for the specific polymer/substrate system. The resultant ceramic-supported polymer (CSP) membrane is a composite structure in which mechanical strength is provided by the ceramic support and the selectivity is determined by the covalently bonded polymer brush layer. Thus, one of the unique attributes of the CSP membrane is that it can be used in environments where the polymer layer is swollen (or even completely miscible) in the mixture to be separated (Castro et al., 1993). It is important to note that the above modification process is carried out under mild conditions (e.g., temperature of about 70°C) and is well suited for large scale commercial application.

In a series of studies, the applicability of a polyvinylpyrrolidone CSP membrane was demonstrated for the treatment of oil-in-water emulsion under a variety of flow conditions (Castro et al.,1996). Improved membrane performance was achieved due to minimization of surface adsorption of the oil components. For the special case of long surface chains, significant additional performance improvement (permeate stream was attained at high Reynolds numbers. At the high Reynolds number condition, shear-induced deformation of the terminally anchored polymer chains and as a consequence the screening of the pore entry, resulted in improved permeate quality. Current studies are focused on the optimization of the polymer surface layer and quantification of chemical and hydrodynamic polymer-emulsion interactions.

Pervaporation is another promising application of CSP membranes. An approach was developed to enable the selection of the specific polymer phase for a given separation task. In a series of studies it was shown, as predicted theoretically, that a Poly(vinyl acetate) CSP (PVAc/CSP) membrane can be used to separate and recover trichloroethylene (TCE) and chloroform from aqueous solutions. Enrichment factors ranging from 60-110 were obtained for the removal of TCE and chloroform from solutions near saturation down to the few parts per million range. These experiments with a tubular CSP membrane (10 cm long and 1 cm internal diameter) demonstrated that, for a single-pass operation of feed solutions of concentrations above about 200 ppm, a pure organic solvent phase was recovered with an additional organic saturated aqueous phase which can be recycled to the feed. The resistance to transport across the CSP membrane was shown to be controlled solely by the concentration boundary layer in the tube-side hydrodynamic; the boundary layer resistance decreased markedly as the tube-side Reynolds number increased to the turbulent regime. The enrichment factor (total solute concentration in permeate/solute concentration in feed) was shown to increase with the polymer graft density. It was shown, for the first time, that pervaporation is possible (with CSP membranes) even with membrane pores much larger than the solute.

The CSP membrane technology has tremendous potential for advancing the use of membranes not only for water treatment applications but also for the separation of organic/organic liquid mixtures. The CSP membranes are ready for testing and scale-up for field applications. In order to adapt the CSP membranes for a large scale applications one could utilize available arrays of tubular membranes or a multichannel membrane assembly. The graft-polymerization procedure will have to be tested for the larger scale modification and adapted as necessary. The testing of large scale application would require the development of a pilot-scale demonstration project which is necessary for further development work. Such an endeavor, however, is beyond the scope of the present project and could be best achieved through a follow-up demonstration project. For the third year of the present project, further experimental and theoretical development work is planned to optimize the CSP membrane fabrication process.

References

Castro, R.P., H.G. Monbouquette and Y. Cohen, “Polyvinylpyrrolidone-Silica Membranes for the Treatment of Oil-in-Water Emulsions”,” J. Membrane Science, 115, 179-187 (1996).

Castro, R.P., H.G. Monbouquette, and Y. Cohen and R. Castro, “The Permeability of Surface Modified Porous Silica Membranes,” Journal Membrane Science, 84, 151-160 (1993).

Chaimberg, M. and Y. Cohen, “The Kinetics of Graft Polymerization onto Silica Substrates,” AIChE Journal, 40, 294-311 (1994).

Planned Activities

Although a reasonable data set now exist that demonstrates the potential of CSP membranes, the optimization of membrane performance will require additional information on the precise surface morphology and its correlation with graft polymerization conditions and the surface properties of the support. In addition, better understanding of solute-brush layer interactions are needed in order to optimize membrane performance for both filtration and pervaporation applications. Several activities are planned for the third year of the project which include surface characterization by a variety of techniques (e.g., atomic force microscopy, internal reflection IR using model surfaces, contact angle measurements). We also hope to conduct a series of surface characterization studies to determine segment density distribution in collaboration with scientists from NIST. Finally, our pervaporation studies will be extended to demonstrate organic-organic separations and to establish a quantitative relationship between membrane selectivity and polymer layer morphology.

Other Access To Information

Additional information can be found at **http://www.polysep.ucla.edu/**

Design and Construction of Deinococcus radiodurans for Biodegradation of Organic Toxins at Radioactive DOE Waste Sites

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Research Objective

A 1992 survey of DOE waste sites indicates that about 32% of soils and 45% of groundwaters at these sites contain radionuclides and metals plus an organic toxin class. The most commonly reported combinations of these hazardous compounds being radionuclides and metals (e.g., U, Pu, Cs, Pb, Cr, As) plus chlorinated hydrocarbons (e.g., trichloroethylene), fuel hydrocarbons (e.g., toluene), or polychlorinated biphenyls (e.g., Arochlor 1248). These wastes are some of the most hazardous pollutants and pose an increasing risk to human health as they leach into the environment.

The objective of this research is to develop novel organisms, that are highly resistant to radiation and the toxic effects of metals and radionuclides, for in-situ bioremediation of organic toxins. Few organisms exist that are able to remediate such environmental organic pollutants, and among those that can, the bacteria belonging to the genus Pseudomonas are the most characterized. Unfortunately, these bacteria are very radiation sensitive. For example, Pseudomonas spp. is even more sensitive than Escherichia coli and, thus, is not suitable as a bioremediation host in environments subjected to radiation. By contrast, D. radiodurans, a natural soil bacterium, is the most radiation resistant organism yet discovered; it is several thousand times more resistant to ionizing radiation than Pseudomonas. The sophisticated gene transfer and expression systems we have developed for D. radiodurans over the last eight years make this organism an ideal candidate for high-level expression of genes that degrade organic toxins, in radioactive environments. Our ultimate aim is to develop organisms and approaches that will be useful for remediating the large variety of toxic organic compounds found in DOE waste sites that are too radioactive to support other bioremediation organisms.

Research Progress and Implications

This report summarizes work after the first 6 months of a 3-year project. The work described here has been submitted for publication. Thousands of high priority waste sites around the world contain mixtures of toxic chlorinated solvents, hydrocarbon solvents and radionuclides. Because of the inherent danger and expense of cleaning up such wastes by physicochemical methods, other methods are being pursued for cleanup of those sites. One alternative method could be to engineer radiation resistant microbes that have the ability to degrade or transform those wastes to less hazardous mixtures. Here, we report the construction and characterization of recombinant Deinococcus radiodurans, the most radiation resistant organism known, expressing toluene dioxygenase (TDO).

Genes encoding TDO (todC1C2BA, cloned form Pseudomonas putida) were chosen for expression in D. radiodurans because TDO is prototypic of a large class of bacterial dioxygenases and has a broad substrate range that includes compounds present at sites containing organic and radioactive mixed wastes. Furthermore, TDO is comprised of four protein components with their attendant metal and organic cofactors and, thus, its successful expression in D. radiodurans suggests that many less complex biodegradative enzyme systems could be expressed.

Sequence Analysis of the D. radiodurans Genome: The nearly completed D. radiodurans genomic DNA sequence was searched for similarity to TDO sequences using the Basic Local Alignment Search Tool (BLAST). No D. radiodurans sequences were found to have significant homology at the

DNA level nor at the translated peptide level, suggesting that a TDO homolog does not exist in D. radiodurans strain R1 (wildtype).

Construction of D. radiodurans Strains MD560 and MD417: The todC1C2BA genes cloned into D. radiodurans (strain MD560) are constitutively expressed to make functional TDO. D. radiodurans strains R1 (wildtype), MD417 (control strain with vector sequences lacking tod genes, tod-) and MD560 (tod+) were incubated with indole and only strain MD560 yielded indigo. Incubation of 1.5 x 10+9 cells/ml of strain MD560 resulted in complete degradation of 25 nmole/ml of toluene and chlorobenzene in 30 minutes and at near equal rates. A similar reaction with 25 nmole/ml 4-dichloro-1-butene resulted in oxidation of about 40% of the substrate in 80 minutes. Incubations of overnight grown cultures of MD560 (1 x 10+8 cells/ml) with chlorobenzene, toluene and 3,4-dichloro-1-butene yielded the anticipated diol products, as determined by GC/MS analysis of culture supernatant extracts. All of the in vivo products were identical by GC/MS analysis to products obtained in vitro using purified toluene dioxygenase. Although chlorobenzene, toluene, and 3,4-dichloro-1-butene were detectably oxidized by headspace analysis, 25 nmole/ml trichloroethylene (TCE), a substrate known to inactivate TDO, was not detectably oxidized under these conditions. However, incubation of MD560 with volatile ^{14}C-TCE yielded a detectable increase in ^{14}C-nonvolatile material that was associated with the cells. This was consistent with previous studies in vivo and in vitro in which ^{14}C-TCE oxidation inactivates TDO and becomes covalently attached to cell materials. Strain MD417, lacking tod genes, was uniformly negative in the metabolism of all the TDO substrates tested.

In strain MD560, the toluene dioxygenase expression is low level constitutive (TDO concentration is undeterminable by SDS-PAGE). Our closest comparison was with E. coli DTG351 which is also constitutive, but is plasmid encoded and not chromosomal, like MD560. We have determined that the oxidation rate of ^{14}C -toluene to non volatile ^{14}C -labeled products by strain MD560 is about half of that observed for E. coli strain DTG351.

Resistance of D. radiodurans to Toluene and TCE: The cell envelope of D. radiodurans includes an outer and inner lipid membrane that surrounds the cell wall. It was unknown before this study if the membrane architecture of this organism might result in sensitivity or resistance to organic solvents. Organic solvents are generally toxic to bacteria by making their membranes porous. Toluene and TCE are two of the most common organopollutants at radioactive DOE waste sites; toluene has been reported as high as 26 mg/L groundwater and 2,000 mg/Kg soil, and TCE as high as 1,000 mg/L and 12,000 mg/Kg. Our work shows that D. radiodurans wildtype and toluene metabolizing strains were all found to be naturally tolerant to toluene and TCE groundwater concentrations well above those found at most sites, and resistant to about half the highest toluene concentrations reported in contaminated soils.

Before this work, no studies regarding D. radiodurans' growth in the presence of continual radiation had been reported to our knowledge. Likewise, information regarding effects of radiation on D. radiodurans' growth and protein expression, or solvent effects, were not available. Our work strongly supports the idea that recombinant D. radiodurans strains can be constructed for biodegradation in radioactive aqueous/organic mixed wastes.

Reference

Lange C., L. Wackett, K. Minton, and M.J. Daly. 1998. Construction and characterization of recombinant Deinococcus radiodurans for organopollutant degradation in radioactive mixed waste environments, submitted.

Planned Activities

Our ultimate aim is to design novel D. radiodurans strains that can not only degrade organic toxins, but also derive carbon and energy from these compounds while at the same time surviving the effects of co-contaminating toxic metals and radionuclides. To this end, we will be working on the following projects over the next year:

1) Cloning the companion genes in the toluene catabolic pathway into D. radiodurans strain MD560 (see Research Progress). Once cloned, we intend to test the expression of those genes and determine if aromatic compounds can be catabolized to products that can be fed into the

organism's carbon-assimilating and energy-yielding pathways. A parallel investigation of ours is now sytematically mapping D. radiodurans' metabolic pathways by a combination of genomic informatics and biochemical/growth assays.

2) Since DOE radioactive sites contain high concentrations of toxic metals, D. radiodurans will have to be designed for resistance to metals (e.g., U, Co, Cd, As, Zn). We have cloned the Desulfovibrio vulgaris cytC3 gene into D. radiodurnas and have obtained a series of metal resistance genes (e.g., cnr and czc; Alcaligenes eutrophus) for introduction into our strains. Metal resistance profiles of the engineered strains will be determined.
3) We have developed an assay for D. radiodurans using a newly engineered strain that can distinguish between lethality as the result of DNA damage and lethality that is the result of cellular toxification by non-DNA damaging agents (such as solvent toxicity). This assay will be used to assess the relative toxicity of organics, metals and their potentially interacting combinations in simulated DOE waste soils. Results of this assay may help us to better understand and engineer the organism for survival in actual DOE waste environments.

Molecular Profiling of Microbial Communities from Contaminated Sources: Use of Subtractive Cloning Methods and rDNA Spacer Sequences

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Research Objective

The major objective of the research is to provide appropriate sequences and to assemble a high-density DNA array of oligonucleotides that can be used for rapid profiling of microbial populations from polluted areas. The sequences to be assigned to the DNA array are chosen from from cloned genomic DNA sequences (the ribosomal operon, described below) from groundwater at DOE sites containing organic solvents. The sites, Hanford Nuclear Plant and Lawrence Livermore Site 300, have well characterized pollutant histories, which have been provided by our collaborators.

Research Progress and Implications

At this mid-point of the project, over 60 unique sequence classes of intergenic spacer region have been idedntified from the first sample site. The use of these sequences as hybridization probes, and their frequency of occurrence, allow a clear distinction between bacterial communities before and after remediation by acetate/nitrate pumping. We have developed the hybridization conditions for identifying PCR products in a 96 well format, a versatile alignment and visualization program (acronym: MALIGN) developed by Dr. Dennis Maeder, has been used to align the ISRs, which are variable in length and sometimes in position of the tRNAs. Finally, in collaboration with Dr. W. Chen and Dr. J. Zhou at ORNL, we have significant evidence that mass spectrometer analysis can be used to determine the lengths of PCR amplified intergenic spacer DNA.

We are using standard DNA isolation, polymerase chain reaction (PCR), cloning, and sequence analysis methods in 96-well microtiter plate formats in order to reduce the cost and time necessary for sequencing hundreds of bacterial intergenic spacer regions (ISRs). ISRs have been amplified by PCR using generic 16s (5 forward) and 23s (5 reverse) primers using DNA from well samples from the Hanford site, representing upper and lower ground water levels, early, mid., and late in the

enrichment/pumping procedure used in bioremediation. Libraries of these ISRs have been sequenced, and the sequences aligned and sorted into bins. Bins are described by type (best blast species) and structure of the ISR. We have 60^{+} unique sequences (=bins) at present, after sequencing more than 300 ISR sequences. Figure 1 shows the structure of the most common type of ISR found in our samples. Other types are described relative to this model.

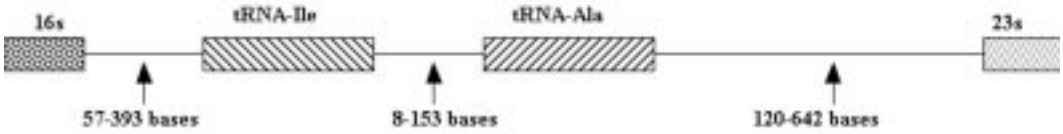

Figure 1. **Structure of the most common (67%) ISRs found in Hanford groundwater samples. Only 9% of our clones have no tRNAs (ISR ~200 bases); the remaining 24% have only an an Ile tRNA or Glu tRNA, or else the order of Ala tRNA and Ile tRNA is reversed.**

Hypervariable stretches of the ISRs, in the inter-tRNA (itRNA) region, have been synthesized and hybridized against synthetic, labelled templates corresponding to the opposite strand, in collaboration with Molecular Tool, Inc, in a 96-well microtiter plate hybridization format (Figure 2). We are collaborating with Dr. Mary Lowe at Loyola College, MD on a particle hybridization/cell sorting/flow cytometry method for fast, iterative hybridization.

Eleven of the unique sequence classes align with Pseudomonad ISRs. Other sequences are related to *Thiobacillus cuprinus, T. ferroxidans, Agrobacterium vitis, Xylophilus ampelinus, Bradyrhizobium japonicum, Bartonella bacilliformis, Xanthomonas maltophilia, Prevotella ruminicola, Cryptomonas* sp., and *E. coli* . ISRs that are 95% identical in sequence are considered to be from the same species. ISRs that are 85% similar are tentatively assigned to different strains, and if their distribution is of interest (for example, if the occurrence of the strains is noncongruent), we examine them in more detail.

The development of a large sequence database of ribosomal 16s and ISR sequences will reflect genetic diversity and selection at the contaminated sites. The differences in diversity at Hanford sites before and after remediation echo the effects of environmental pollution on plankton and vertebrates. Sequence information and community dynamics will allow better interpretation of pollution history and the progression of degradation.

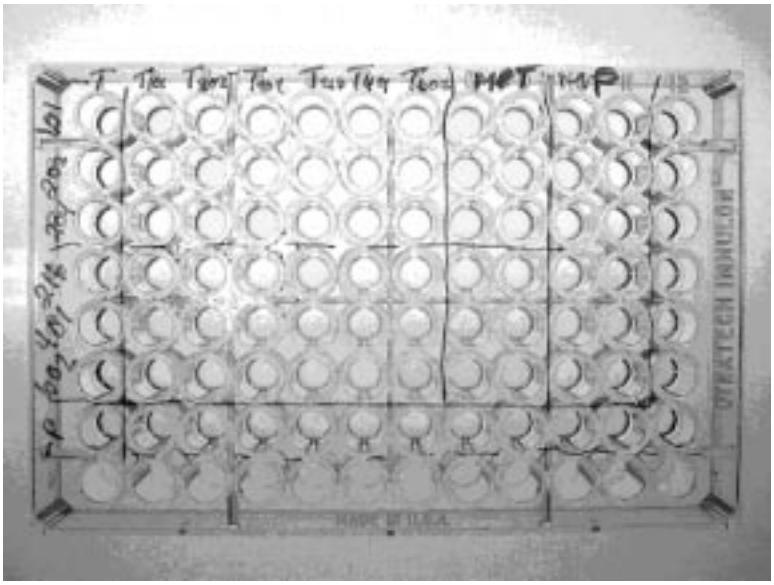

Figure 2. Hybridization of itRNAs vs synthetic templates. Fluoresceinated templates were hybridized to synthetic itRNA primers immobilized on the bottoms of the wells.

Planned Activities

Ground water from monitor wells within the LLNL Building 834 Area having varying amounts of VOC contamination are being sampled quarterly for microbiological assessment. Five monitor wells have been selected for this study based on their VOC concentrations. Two of the wells selected (W-834-D3, and W-834-D14) have high VOC concentrations, predominantly TCE, in excess of 100,000 µg/L. A third well (W-834-B3), has lower levels of VOCs, around 10,000 µg/L, which is almost entirely composed of 1,2-DCE. All three of these wells have dedicated extraction pumps used for the treatment facility. The two remaining wells selected (W-834-S6, and W-834-T5) have not historically contained any VOC compounds (clean wells, control populations). All five wells selected are installed within the same hydrologic unit.

We will shortly test the environmental DNA from LLNL (as a PCR amplified sample) in an inter-site hybridization experiment against the sequences from the Hanford sites to find out how much overlap there is in microbial community composition. We will also hybridize against sequences described in the NCBI and Deep Subsurface databases, to probe for sequences without the intermediate cloning step. This new sampling site is an ongoing project for LLNL and DOE and will provide us with progressive sampling to test our arrays, particle detection methods, to follow the time-course of contamination and natural remediation effects on bacterial groundwater communities.

Other Access To Information

Brown, D.C, R.H. Shanks, D. Maeder, M.L. Lowe, F.J. Brockman, and Robb, F.T. Profiling microbial communities in polluted ground water: Effects of bioremediation. In prep. for Applied and Environmental Microbiology.

Web Site

http://comb5-156.umbi.umd.edu/bags.html (local ISR database)

Genetic Analysis of Stress Responses in Soil Bacteria for Enhanced Bioremediation of Mixed Contaminants

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Research Objective

To realize the full potential of bioremediation, the individual bacterial responses to the stresses (lack of nutrients or oxygen; mixed pollutants) encountered at contaminated sites must be understood. This information can then be extrapolated to field applications using indigenous bacteria or genetically engineered micro-organisms. Studying bacterial response to stresses presents an opportunity for improving bioremediation strategies, both with indigenous populations and genetically engineered microbes, and should contribute to environmental management and restoration goals.

Enhancing in-situ removal of hazardous wastes by stimulating the growth of indigenous bacteria with nutrients has been demonstrated. But how much and how often to apply these supplements has been difficult to determine, and controlled and reproducible degradation of pollutants in the environment has not yet been achieved.

Research Progress and Implications

As of May 31st 1998, this report summarizes work after 17 months of a 36 month project.

The starvation responses of Sphingomonas aromaticivorans F199 were analyzed. Using S. aromaticivorans as a model, the effects of adding nutrient to starved cells were investigated in terms of protein and gene expression. Cells were starved in reconstituted well water without carbon and nitrogen sources for nine months. Nutrient (TGY medium) was added to the starved cell, and proteins were extracted from the cell culture after 4, 8, and 24 hours. Only a few major proteins were present and few changes were detectable four hours after the nutrient was added, but several prominent proteins appeared after eight hours, suggesting that there is a lag time before the starved cells respond to the nutrient. These identified proteins may be useful for monitoring the bioremediation process during biostimulation with nutrient supplements.

Twenty-four hours after nutrient was added, the size of rRNA molecules of recovery cells had increased. The rRNA may have undergone fragmentation under starvation conditions. Efforts are focused on determining the sequences of the rRNA from starved and recovery cells. Comparing these sequences may enable scientists to develop oligonucleotide probes to monitor the number of recovery cells that are metabolically active during bioremediation.

Few genes on the catabolic plasmid pNL1, which encodes genes for the degradation of compounds such as naphthalene, biphenyl and xylene, are still active in the starved cells. These genes responded more robustly to the nutrient. Apparently, most of the catabolic genes were not activated by the nutrient, suggesting that, although the nutrient supplement stimulates the growth of the bacteria, it does not necessarily stimulate the biodegradative activities of the bacteria.

The stress responses of Deinococcus radiodurans R1 were analyzed. RNA was harvested from cells grown in starvation media. RAP-PCR was performed, and 12 tentative differentially expressed genes were identified. Sequence analysis revealed that one of the identified genes has a significant sequence identity with transposase. Experiments are in progress to confirm stress inducibility of that gene. The promoter of that gene may be useful in engineering D. radiodurans for the degradation of TCE under starvation or environmental stress conditions.

Genetic engineering methods are being developed for S. aromaticivorans F199, which has become tetracycline-resistant for better performance in bioremediation. It was successfully transformed using the electroporation method. Using this tetracycline-resistant strain, transposon elements were delivered into the chromosome via conjugation.

A modification of duplication insertion has been developed to create insertional mutations in the D. radiodurans genome, called duplication inactivation. Several approaches have been pursued to identify appropriate promoters for expression of the tbu gene in D. radiodurans. The first gene identified, sigma factor, encodes an important regulatory protein. RNA polymerase, the enzyme complex responsible for transcription, is composed of multiple subunits, including the sigma factor. Experiments have been initiated to determine the expression pattern of the other four putative stress factors. Promoters from these genes will be used to express toluene 3-monooxygenase enzyme complex in D. radiodurans for degradation of TCE under starvation or environmental stress conditions.

Investigations have also been focused on the katA gene, which encodes the major catalase enzyme. We investigated whether the katA promoter is good for the expression of Tbu under nutrient-limiting conditions. The role of katA in radiation and peroxide resistance was investigated. The findings suggest that the major catalase is involved in the extreme hydrogen peroxide resistance of D. radiodurans and to a lesser extent is involved in ionizing radiation resistance. Thus, expressing heterologous genes useful for bioremediation with katA promoter might be ideal for bioremediation at the mixed-contaminant site with radionuclides.

Planned Activities

1. Determine the complete sequences of rRNA of starved cells and recovery cells to develop oligonucleotide probes for monitoring the physiological state of soil bacteria.
2. Study stress responses to trichloroethylene, a major contaminant at DOE sites.

3. Because over-expressing robA or pspA genes in Escherichia coli can enhance its resistance to metal and organic solvent, we will attempt to over-express these genes in both S. aromaticivorans and D. radiodurans.

4. Further analyze all Deinococcus strains expressing Tbu, including Northern analysis, timing of expression, and analysis of these strains' degradative ability for trichloroethylene and toluene in pure culture studies.

Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media

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Research Objective

The objective of this research is to determine the relationship between of biologically active contaminant degradation zones in a fractured, subsurface medium and vertical geological heterogeneities. The research is being performed on samples collected from the Test Area North (TAN) site at the Idaho National Engineering and Environmental Laboratory (INEEL) where a dissolved trichloroethylene (TCE) plume is migrating in the basalts and interbed sediments of the Eastern Snake River Plain (ESRP) aquifer. Results are leading to an enhanced understanding of the constraints placed on the activities and distribution of TCE-degrading organisms by the geochemical and hydrological environment. This understanding allows better decisions to be made regarding the use of remedial technologies such as natural attenuation and in-situ bioremediation at geologically complex waste sites. Through this research, investigations conducted by the DOE Subsurface Science Program at TAN have been extended in order to develop a mechanistic understanding of the coupled geomicrobial and hydrogeochemical processes that are necessary to predict field-scale intrinsic degradation rates of TCE. The research objective is being accomplished by characterizing paired cores and water samples from boreholes located in differing geochemical and flow environments within the plume. Analysis of these samples will allow the determination of the spatial correlation between microbial degradation and preferred flow paths for the contaminant and required electron donors and acceptors. A combination of traditional microbiological methods (e.g., enrichments) and molecular tools are being used to characterize the indigenous microbial communities.

Research Progress and Implications

This report summarizes work conducted after 1.5 years of a three year project. As of May 1998, subsurface basalt and sediment cores had been collected for microbiological and chemical analyses from the saturated zone in three coreholes at TAN. Core materials were acquired from ca. 67 m

below land surface (BLS) to 134 m BLS. One corehole (TAN-37) is located proximal (40 m) to the injection well and is in a zone that is heavily influenced by the waste (2000-3000 ppb dissolved TCE) while a second hole, TAN-33, is located more distally (305 m) where dissolved TCE is ca. 900 ppb. The third corehole, TAN-48, is even more distant (600 m) where the dissolved TCE is ca. 100 ppb. The aquifer consists of multiple basalt flows where dense fracture networks conduct the groundwater. At the upper and lower end of the range cored are two sedimentary interbeds. Microbiological analyses conducted on pared core samples include biomass and community structure by phospholipid fatty acid (PLFA) analyses; cultural enumerations of methanotrophs, propanotrophs, phenol-oxidizers, ammonia oxidizers, iron reducers, sulfate reducers, methanogens and fermenters; community-level physiological profiles (CLPP); 16s rRNA sequencing of polymerase chain reaction (PCR) products, denaturing gradient gel electrophoresis (DGGE) analysis of extracted DNA and acetate mineralization. Data from intentionally introduced tracers (microspheres and perfluorocarbons) indicated several orders of magnitude reduction in potential contaminants was achieved by paring the cores. Comparison of the both whole communities and isolates from the core and drilling fluid corroborated the defensibility of the cores.

TCE concentrations in cores samples from TAN-33 were consistently low (< 6 ppb) whereas higher values were detected in samples from TAN-37 (as high as 25 ppb). That these values for TCE in basalt are so low relative to the concentrations of TCE evident in groundwater at these locations is corroborated by evidence of low adsorption of TCE on basalt (Ingram et al. Surface Chemistry of Subsurface Basalt; OBER; Wolf-Broido Initiative). The TCE concentrations in TAN-33 cores peaked at 103 m; just above a zone of pervasive fractures that correspond to a perceived interflow zone. In TAN-37, the highest TCE values in the cores occurred at depths between 68 and 79 m, near the top of the aquifer at this location. These data are consistent with cross-hole seismic tomography conducted in TAN-37 and neighboring wells which suggest primary flowpaths may exist at ca. 74 m (see EMSP progress report submitted by E Majer entitled: “Subsurface High Resolution Definition of Subsurface Heterogeneity for Understanding the Biodynamics of Natural Field Systems: Advancing the Ability for Scaling to Field Conditions”).

Microbial biomass in the basalt from the corehole at intermediate distance from the injection well (TAN-33) was at the limit of detection for most assays; minimal acetate mineralization was detected for select samples. Aerobic heterotrophs were cultured on oligotrophic liquid media (0 to 10E4 cells/g) and phenol-oxidizers (< 10E2 cells/g), methanotrophs (< cells 20/g), and dissimilatory iron reducing bacteria were present in some core samples. On the other hand, basalt from TAN-37, proximal to the injection well, showed measurable biomass by PLFA (ca. 3 pmol/g) and much higher levels of acetate mineralization. Higher numbers of the different physiological types of microorganisms were enriched in all samples from TAN-37 relative to those from TAN-33. The following order of prevalence was discernible in enumerations of specific microbial types in cores from TAN-37: phenol oxidizers (< 10E5 cells/g) > propanotrophs (< 10E4 cells/g) >> methanotrophs (< 10E2 cells/g) >> nitrifiers. Furthermore, evidence from TAN-37 cores suggests that samples from interflow zones (strata that represent the boundary of two adjacent basalt flows) may contain higher numbers of microorganisms than samples obtained from within a single basalt flow. If true, this is consistent with the hypothesis that the interflow zones which are highly fractured and contain basalt rubble are the preferred flow paths for contaminants and that these zones also support a more robust microbial community. Comparison of the data from TAN-33 and TAN-37 indicate that bacteria associated with basalt may be present in low numbers in pristine areas of the aquifer while a substantial stimulation of similar types of organisms may result from organic contamination.

Microbial DNA was extracted from selected TAN-33 and TAN-37 samples and amplified using PCR with eubacterial and archaeal primers. TAN-33 samples did not yield visible PCR bands but when spiked with as few as 10E4 cells/g samples PCR bands were apparent. Invisible PCR bands from two of the TAN-33 samples along with a full procedural blank (processed without basalt) were cloned and a subset of the clones was submitted to Amplified Ribosomal DNA Restriction Analysis (ARDRA). Six ARDRA types (all eubacterial) were identified from the 113.3 m sample and three ARDRA types (all eubacterial) were identified from the 125.4 m sample. Basic Local Alignment Search Tool (BLAST) was used to compare the sequences of these eubacterial clones to that of known microorganisms. Most of the sequences that resulted from these clones were approximately

90% similar to known eubacterial sequences. Extractions from selected TAN-37 samples indicate much higher levels of DNA than in TAN-33 samples. Eubacterial PCR bands were recovered from all of the samples that were amplified except the combusted basalt control sample. Only one of the ten samples yielded an archaea PCR band. Cloning and sequencing of these PCR bands indicate a diversity of microorganisms in the samples from the top of the aquifer in TAN-37 including types that are common in soil environments (e.g., Acinetobacter, Pseudomonas, and actinomycetes).

Preliminary determination of microbial diversity in TAN-37 samples from 63.5 m (basalt; top of the aquifer) and 125.7 m (sediment interbed; below of contaminated strata) were obtained using DGGE. The diversity profiles were different for the two samples, although they did share three common banding patterns. Both samples had about eight different bands, representative of eight putative different 16S rDNA fragments. Initial recovery and sequencing of one of the dominant bands common to both samples revealed that this product was most closely related to members of Acinetobacter. This genus is consistent with the results obtained from the clone library developed for TAN-37 samples that came from 63.5 to 78.8 m depths. Most Acinetobacter spp. are nutritionally diverse and common inhabitants of soils.

This EMSP research will help address EM-40 needs in the cleanup of the waste plume in the groundwater at TAN by: 1) determining the specific vertical location of contaminants in the ESRP aquifer, 2) establishing the presence and distribution of naturally occurring microbial communities that are capable of contaminant degradation, and 3) determining the abiotic conditions (chemical and physical) under which these microorganisms are active in the degradation of the TCE. Ultimately, by acquiring data to allow estimates of the natural rates of waste remediation in the aquifer at TAN, this EMSP research will assist EM-40 and regulatory agencies that have oversight of the cleanup activities, in determining where aggressive remediation must be conducted and where it is likely that natural attenuation of the contaminants will occur.

Planned Activities

Multi-level sampler (MLS) for discrete static sampling of aquifer microbiological and chemical characteristics will be retrieved from TAN-33 (Jun 98).

Initiate MLS study in TAN-37 (Aug 98).

Complete microbiological and chemical analyses on samples from TAN-48 (most distal corehole) (Sep 98).

Complete microbiological and chemical analyses of MLS samples from TAN-33 (Oct 98).

MLS retrieved from TAN-37 (Apr 99).

TAN-33 MLS data analysis completed allowing: 1) comparison of MLS data to that obtained from cores at the same vertical location in the borehole, 2) estimation of importance of attached vs. unattached microbial communities in the context of contaminant degradation, and 3) verification of distinctive microbial communities according to geohydrological environment (May 99).

Complete microbiological and chemical analyses of MLS samples from TAN-37 (Aug 99).

Deduction of the natural rates of waste remediation in the aquifer at TAN (Sep 99).

Dynamics of Coupled Contaminant and Microbial Transport in Heterogeneous Porous Media

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Research Objective

Dynamic microbial attachment/detachment occurs in subsurface systems in response to changing environmental conditions caused by contaminant movement and degradation. Understanding the environmental conditions and mechanisms by which anaerobic bacteria partition between aqueous and solid phases is a critical requirement for designing and evaluating in-situ bioremediation efforts. This interdisciplinary research project will provide fundamental information on the attachment/ detachment dynamics of anaerobic bacteria in heterogeneous porous media under growth and growth-limiting conditions. Experiments will provide information on passive and active attachment/ detachment mechanisms used by growing anaerobes capable of reductive dechlorination. Theoretical representations of these attachment/detachment mechanisms will be incorporated into existing flow and transport models that incorporate heterogeneity effects and can be used to predict behavior at field scales. These mechanistic-based models will be tested against experimental data provided through controlled laboratory experiments in heterogeneous porous media in large (meter-scale) 2-D flow cells. In addition to a mechanistic-based predictive model, this research will lead to new theories for the transient spatial distribution of microbial populations and contaminant plumes in heterogeneous porous media, improving our capability for designing staged remediation strategies for dealing with mixed contaminants.

Research Progress and Implications

The central challenge of in-situ remediation strategies is the control of the transient spatial distribution of contaminants and remediation reagents (e.g., nutrients or microorganisms) in the presence of natural physical and chemical heterogeneities. Currently available predictive tools rely almost exclusively on the representation of passive attachment/detachment processes (e.g., filtration, sedimentation) with the bacterium treated as an inert biocolloid. One of the most intractable aspects of bioreactive transport, however, is active microbial partitioning (e.g., attachment/ detachment) under growth and transport in physically and chemically heterogeneous systems. Active attachment/ detachment is associated with microbial physiologic response to changes in local aqueous concentrations of nutrients and electron-acceptors: this process is treated rarely in field-scale bacterial transport theories, and not at all in available predictive tools.

Understanding coupled contaminant and bacterial transport in real media is critical to the success of potential future bioremediation/biobarrier strategies at DOE sites. Disposal of chlorinated hydrocarbons has generated extensive contaminant plumes in sand/gravel aquifers at DOE's Savannah River Site (SRS) in South Carolina and Paducah Gaseous Diffusion Plant (PGDP) in Kentucky, and such organic solutes interact with natural environments in coupled complex ways that have serious ramifications for remediation. For example, during the SRS in-situ bioremediation demonstration, 90% of the increase in methanotroph biomass arising from degradation of trichloroethylene (TCE) partitioned into the aqueous phase. Initially, this methanotroph population was primarily attached to solid surfaces. If this partitioning behavior during bioremediation were understood and could be predicted, the knowledge could be exploited to effectively distribute the biomass across a contaminated area and to plan an injection network so as to minimize costly well construction and dampen or

eliminate microbially-induced reductions in hydraulic conductivity. This basic knowledge on the transport response of microorganisms is required for any subsurface remediation involving microbes, including staged approaches that sequentially degrade and immobilize multiple contaminants. Staged approaches (temporal or spatial) can exploit the different transport properties of distinct microbial populations and are especially well suited to DOE mixed contaminant problems.

Research Progress

The work on this project is being coordinated among six different investigators at five different institutions, Madilyn Fletcher (University of South Carolina), John Cushman (Purdue University), Timothy Ginn (University of California, Davis), David Boone (Oregon Graduate Institute), and Ellyn Murphy and Donald Friedrich (Pacific Northwest National Laboratory). In addition, three post doctoral students have been supported by this project, Paula van Schie (USC), Robert Smits (Purdue), and Zheming Wang (PNNL).

Adhesion Behavior of Anaerobes: Thus far, the adhesion characteristics of two anaerobes (D. tiedjei and Desulfovibrio) have been tested, with greatest emphasis on D. tiedjei. Results have demonstrated interesting contrasts among these strains, which will be useful when designing experiments for consortium transport. First, the three organisms demonstrate very different attachment properties: D. tiedjei adheres in highest numbers, whereas Desulfovibrio G11 adheres only when it is actively. Second, the adhesion of D. tiedjei remains the same whether the cells are actively growing or starved, whereas that of Desulfovibrio is reduced when the cells are starved.

Additional features of the attachment of these organisms will increase the complexity of modeling their transport. Both D. tiedjei and Desulfovibrio G11 demonstrate significant detachment rates, after initial attachment has occurred. Also, sedimentation of cells has been found to influence attachment numbers on the top-side of surfaces. Thus, cell mass and sedimentation must be accounted for in model development, particularly for the relatively large D. tiedjei.

Stochastic Representations of Bacterial Transport in Porous Media: A microflow chamber is being constructed at PNNL for use with the confocal microscope to determine the residence time of anaerobic bacteria on porous media. To quantitatively evaluate these experiments, a model of microbial dynamics in the porous media has been developed. This multidi-men-sional mathematical model depicts sticky Brownian motion with drift, as a general representation of microbial transport with attachment/detachment. A sticky Brownian motion with drift allows a particle (e.g., microbe) to diffuse by classical Brownian motion in a pressure-induced convective field, except when it hits a wall. When it hits the wall it sticks for a random period of time, which is dictated by a probabilistic stickiness condition. Therefore, this model predicts the location in space of a microorganism as a function of the random force, the drift, and the boundary force. The random force is the diffusive, Brownian-like motion (e.g., motility) and kinematic dispersion in porous media; drift is the convection due to water flow; and the boundary force is the sticking probability dependent on space. This pore-scale model has been successfully upscaled to that of a homogeneous porous medium via a central limit argument for continuous ergodic Markov processes.

In Situ Spectroscopy: A laser and fiber optic system has been constructed to observe real-time biomass distribution in porous media. This system takes advantage of the natural fluorescent properties of methanogens (e.g., cofactor F420) or genetically-engineered microorganisms containing a green fluorescent protein. The prototype system has been tested with microspheres which fluoresce in the blue region like the methanogens and with Pseudomonas cepacia containing the green fluorescent protein. As the pulse of microspheres move along the length of the column some tailing is observed and an increase in effective macrodispersion with increasing distance along the column, is also observed. The characteristics of the interior breakthrough curves are consistent with the breakthrough curve at the end of the column suggesting that the laser fiber optic system is observing a “representative” interior cross-section of the column. This system will next be implemented in the flow cell.

Design of Flow Cell Experiments: A numerical representation of a heterogeneous flow field found at the Oyster Site was used to conduct a theoretical experiment to demonstrate the relative effect of dynamic attachment/detachment of bacteria on the degradation of a contaminant plume. We define kinetic attachment/detachment as a partitioning process which arises from cell division and growth

and can be described by determining a forward (attachment) and reverse (detachment) rate kinetic within a growth model. Dynamic attachment/detachment occurs when the forward and reverse rate kinetic varies with metabolic activity. In the mechanistic description, the forward attachment kinetic varies inversely with the specific growth rate, or as growth activity increases, aqueous partitioning of the bacteria increases. Two anaerobic bacteria were used in the consortium, Syntrophobacter which degrades propionate to formate and hydrogen, and D. tiedjei which uses formate as an electron donor and dechlorinates hydrocarbons as an electron acceptor. In one experiment, both Syntrophobacter and D. tiedjei were controlled by kinetic attachment/detachment rates and in the second experiment Syntrophobacter attachment was dynamic (varies with metabolic activity) and D. tiedjei attachment remained kinetic.

A pulse (or plume) of chlorinated hydrocarbon was injected into a heterogeneous flow field and the break-through curves of the contaminants were evaluated. When Syntrophobacter undergoes dynamic attachment/detachment, 58% more of the contaminant is degraded than when the attachment/detachment is kinetic. The enhanced degradation under dynamic conditions is due to the aqueous partitioning of Syntrophobacter which results in an increasing population of this propionate-degrading organism as the contaminant plume moves along the flow path. In this example, the rate of propionate degradation was limiting the metabolic activity of D. tiedjei which promotes the dechlorination reaction. This example clearly illustrates the importance of dynamic attachment/detachment in intrinsic bioremediation.

Planned Activities

The different components of this multidisciplinary research are working towards an integrated intermediate scale flow cell experiment that will take place in FY99. This experiment will be conducted in heterogeneous porous media using a consortia of anaerobic bacteria that collectively dechlorinate hydrocarbons. The information that is currently being collected will be used in the design of this experiment and includes: 1) attachment/detachment kinetics of the different bacterial strains under conditions of growth and starvation; 2) mineralogical controls on the attachment/detachment kinetics of the different strains; 3) mechanistic relationships which describe transport under varying nutrient conditions; 4) in-situ, fiber optic detection of biomass in porous media; 5) growth kinetics of the individual species within the consortia; and 6) upscaling of biogeochemical reactions in heterogeneous porous media.

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Subsurface High Resolution Definition of Subsurface Heterogeneity for Understanding the Biodynamics of Natural Field Systems: Advancing the Ability for Scaling to Field Conditions

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Research Objective

This research is an integrated physical (geophysical and hydrologic) and microbial study using innovative geophysical imaging and microbial characterization methods to identify key scales of physical heterogeneities that affect the biodynamics of natural subsurface environments. Data from controlled laboratory and in-situ experiments at the INEEL Test Area North (TAN) site are being used to determine the dominant physical characteristics (lithologic, structural, and hydrologic) that can be imaged in-situ and correlated with microbial properties. The overall goal of this research is to contribute to the understanding of the interrelationships between transport properties and spatially varying physical, chemical, and microbiological heterogeneity. The outcome will be an improved understanding of the relationship between physical and microbial heterogeneity, thus facilitating the design of bioremediation strategies in similar environments.

Research Progress and Implications

This report summarizes work as of May 1998, the second year of the project. This work is an extension of basic research on natural heterogeneity first initiated within the DOE/OHER Subsurface Science Program (SSP) and is intended to be one of the building blocks of an integrated and collaborative approach with an INEEL/PNNL effort aimed at understanding the effect of physical heterogeneity on transport properties and biodynamics in natural systems. The work is closely integrated with other EMSP projects at INEEL (Rick Colwell et al.) and PNNL (Fred Brockman and Jim Fredrickson).

The research is being carried out in both the laboratory and at DOE field sites under natural conditions. This work addresses issues that will aid in the understanding of what scales one must sample in order to design effective remediation strategies. A critical question is the existence of one or more self-averaging quantities for microbial properties. Stated in another fashion: Are the microbial properties a function of the randomness of the media? If so, what is the size of the representative volume at which the significant properties can be characterized? A specific goal of the research is to advance the understanding of how to effectively use the information from geophysical imaging (i.e., volumetric measurements of physical properties) to predict the effect of physical heterogeneity and fluid transport properties on microbial behavior. A key hypothesis being addressed is that nutrient flux and transport properties are key factors in controlling microbial dynamics. A related hypothesis is that complexity of the subsurface environment is also correlated to the behavior of microorganisms. Geophysics is ideally suited for extrapolating measurements made in a borehole to the large-scale volume away from the hole. With seismic information on location of fractures, layer continuity, layer thickness and other structural and lithologic features, improved predictive models on flow and transport can be developed and applied. This is then correlated to the microbial behavior and distribution. Several different seismic processing approaches are being used to obtain improved information on physical properties controlling transport behavior, including: conventional and advanced ray and waveform tomography; guided/channel waves; scattered energy from voids/high contrast anomalies; and crosswell reflection imaging.

Progress to Date of The Geophysical Imaging

During 1997 the geophysics concentrated on obtaining crosswell seismic data at the sub-meter resolution scale at several wells in the TAN area. The initial crosswell seismic surveys used LBNL's high frequency piezoelectric source which generates energy from 1 kHz to over 5 kHz. Tomographic imaging was carried out for crosswell pairs, T-GRW to TAN-9, TAN-25 to T-GRW, TAN-25 to TAN-26, and TAN-25 to TSF-05. Inversions were produced for the T-GRW to TAN-9 and TAN-25 to T-GRW, TAN-25 to TAN-26, and TAN-25 to TSF-05 well pairs.

Subsurface coverage was good from 64 m (the water table) to over 90 m (depending on well depth). The tomographic imaging allowed identification of velocity heterogeneity in regions as thin as 2 meters and velocity homogeneity over larger regions with sub-meter resolution. From this initial seismic imaging several results were evident. The seismic response of the surveyed area is quite varied, with large changes in seismic velocity and attenuation with depth. From our experience in other fractured environments, this indicates extreme variability in fracture/rock properties and from past experience is an indication of fracture permeability. After completing initial velocity analysis of the piezoelectric data in 1997, we refined the results by including well deviation and anisotropy corrections. A significant result from the initial crosswell surveys was large variations in attenuation. We were not able to propagate the kilohertz frequencies more than about 15 - 20 m between wells, and in some regions the seismic energy was attenuated below measurable levels over distances less than 15 m. Thus, while the piezoelectric source produced high resolution of heterogeneities, the imagable volume was limited by well spacing. We also observed little coherent reflectivity, which focused our study on transmission tomography and guided/channel wave analysis.

In 1998 we wanted to apply crosswell imaging using a well drilled for the EMSP program, TAN-37, which will be used for multi-level sampling and microbial studies. Because the distance from TAN-37 to the nearest wells was over 30m, we felt the piezoelectric source would not be satisfactory.

Instead, we deployed a recently developed borehole seismic source know as an orbital vibrator. The orbital vibrator provides greater seismic energy, although at lower frequencies, and it generates both compressional and shear waves providing the ability for simultaneous P and S-wave imaging. This source, which was originally developed by Conoco, Inc., has to date been used only in oil industry research. Two crosswell surveys were obtained using the orbital vibrator, TAN-37 to TAN-25, and TAN-37 to TAN-30a. To date, we have processed the TAN-37 to TAN-25 data set, obtaining both P and S-wave velocity tomograms. The successful use of this source in the INEEL geologic environment (fractured basalts) allows study of larger well spacings and unique use of P and S-wave comparisons. Although the frequency content is lower (70 to 425 Hz), we were still able to resolve heterogeneous regions 2 to 4 m thick with a resolution of about 1 m. We are also looking at anomalous depths which appear to generate guided waves or interface waves which may be indicative of fracture connectivity between wells. In particular, one apparent guided wave at 74 m in the TAN-37 to TAN-25 well pair agrees with logs showing contaminant flow at that depth in nearby wells. In all well pairs the tomography has given good resolution on structure and possible areas of fast paths.

Progress to Date of Microbial Characterization and Scale Effects

The objective of this work is to characterize small-scale variations in subsurface microbiological properties for the following purposes: providing quantitative estimates (using variogram models) of the spatial variability of these properties; and understanding the relationships between microbiological, physical, and chemical properties (using cross-correlation models). These activities will help identify to what extent geophysical and geochemical properties control the spatial variability of microbiological properties. An additional objective is to determine how the use of different sample supports affects the measurement of microbiological properties. The definition of an appropriate averaging scale is critical in providing more accurate input into predictive models of contaminant transport and will improve the precision of the simulations. The final objective is to quantify changes in the spatial structure and magnitude of microbiological properties following the impingement of a contaminant plume. An associated objective is to determine how the contamination event affects the measurement of microbiological properties at different sample supports.

TAN-33 Rock samples were obtained from one EMSP-funded borehole in FY97. Although we worked closely with personnel at INEEL, it was not possible (given their funding, schedule, and logistical considerations) to obtain the number, type, and quality of rock samples required for meeting the stated objectives. However, in FY98 we are addressing our first two objectives based on sampling and analysis of groundwater from the borehole described above. In TAN-33, after a delay in obtaining samples from the EMSP-funded borehole, we obtained samples from a Subsurface Science Program-funded borehole to refine DNA extraction protocols in basaltic rock material. The TAN-33 borehole was located in a region containing low levels of contamination (less than 0.5 ppm trichloroethylene, TCE). Community DNA was successfully extracted from several of the rock samples, the 16S rRNA genes were amplified and cloned, and phylogenetic analysis was performed.

Compared to TAN-33, the TAN-37 borehole is closer to the source of contamination and contained 5-10 times more TCE. Microbial activity (determined by other investigators) in the TAN-37 borehole was much higher than in the TAN-33 borehole. DNA was extracted and successfully amplified from all rock samples to date; these samples correspond to the depths where the multi-level groundwater sampling will occur in FY98. DNA extraction is being performed on the remaining 15 rock samples from the TAN-37 borehole. Timecourse degradation (1-12 weeks) of ^{14}C-labeled organic substrates (methane and phenol aerobically; lactate and methanol anaerobically) and ^{14}C -trichloroethylene, in the presence and absence of additional inorganic and organic nutrients, was performed on 8 rock samples, and analysis by gas chromatography-gas proportional counting is underway.

Planned Activities

Geophysical Imaging

Although there is strong evidence that the low-velocity zones imaged with the tomography and guided/channel waves are more permeable, further analysis and correlation with other data (well logs, tracer data, etc.) should yield more definitive results on the actual identification of permeable pathways and structure controlling transport. Additional data acquisition is anticipated, focusing on wells used for microbial sampling, TAN-37 and TAN-33.

Characterization of Chemically Modified Hyperthermophilic Enzymes for Chemical Syntheses and Bioremediation Reactions

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Research Objective

Remediation processes frequently involve species possessing limited solubility in water. We are interested in novel strategies that use molecularly-engineered enzymes with enhanced activity and stability for the remediation of recalcitrant compounds in organic media. Organic biocatalysis may be motivated by the nature of the substrate itself, or by augmented mass transport, ease of product recovery, or novel reaction pathways afforded by the organic solvent. However, naturally-occurring enzymes are usually subject to quite limited activity and stability in such organic environments. The objective of the current work is to gain a fundamental understanding of the molecular and catalytic

properties of enzymes that have been chemically-modified so that they are catalytically-active and chemically-thermally-stable in organic solvents. The premise for this study is that highly stable enzymes which are catalytically active in both water and in a range of organic solvents are optimally suited for bioremediation where substrates of interest are more soluble and may be processed with greater specificity in nonaqueous solvents. This bioprocessing system will be assessed using PCB's, DNAPL's and PAH's.

Research Progress and Implications

As of the second of year of a 3-year project, we have obtained promising results for both the demonstration of the proposed remediation strategy and fundamental understanding of the enzymatic catalysis in organic media. In one of our efforts, ligninase (LiP) was modified by poly(ethylene glycol) (PEG) and examined for the degradation of pentachlorophenol (PCP) in water-solvent mixtures. In our other efforts, basic catalytic behaviors of the chemically modified hyperthermophilic metalloenzymes including ferredoxin, hydrogenase and aldehyde oxidoreductase were examined in organic solvents.

I. Biodegradation of PCP by LiP in the Presence of Acetonitrile (MeCN): After initial screening tests with enzymes, modification methods, solvents and substrates, a model reaction system has been selected and characterized to demonstrate the proposed strategy. PCP has been selected as a model contaminant. PCP is only slightly soluble in water, the use of MeCN, however, can effectively increase PCP's solubility. The addition of 15% MeCN enhances the solubility of PCP by over one order of magnitude (from 0.06 to 0.65 mM) as a result of our study. The PEG-modification of ligninase was examined with respect to a few fundamental concerns. It was determined that, by using a free amine group titration method, 12 PEG molecules on average were attached to each LiP under the current modification method. The modification reaction is mild, and no loss in enzyme activity was observed. PEG-LiP was partially soluble in pure MeCN, while no native LiP was found dissolved in MeCN.

The modified LiP was then examined for PCP degradation in the presence of MeCN (up to 30%, v/v). Overall, the activity of PEG-LiP was higher than that of native LiP. Intrinsic activities in solutions containing 1% and 10% MeCN were determined. Interestingly, the activity of PEG-LiP in the presence of 10% MeCN is about 2.5-fold higher than that of native LiP. Experiments with PCP concentrations close to saturation with different amount of MeCN (up to 15%, v/v) were performed. Enzyme and peroxide were added into the reactor continuously by a syringe pump to reduce the enzyme inactivation effect by peroxide. The catalytic efficiency of PEG-LiP for PCP degradation in the presence of 15% (v/v) acetonitrile was 11-fold higher than that of the native enzyme in pure aqueous buffer (480 vs. 44 mole-PCP/mole-LiP h), as a result of the augmentation in both PCP solubility and enzyme activity.

II. Modification of Hydrogenase, Pf Ferredoxin (Fd) and Aldehyde: Oxidoreductase(AOR): The modified enzymes were first characterized by EPR studies. The EPR spectra of the ^{4}Fe- and ^{3}Fe-cluster of the PEG-Fd are similar to those of native Fd in aqueous buffer, although they are not identical. It was also showed that ^{4}Fe cluster in the PEG-Fd becomes oxidized and converted to ^{3}Fe form when dissolved in toluene. These results suggested that oxidation of the Fe-S clusters could be the reason for poor stability/activity of PEG-Fd and PEG-hydrogenase in toluene. The addition of acenaphathalenide was found to be able to prohibit such an oxidation reaction. On the other hand, the hydrogenase EPR signal of the PEG-hydrogenase disappeared in toluene even in the presence of acenaphathalenide, indicating the EPR-active ^{2}Fe-2S cluster was oxidized. PEG-hydrogenase shows reduced EPR spectra in acetonitrile.

The catalytic behaviors of these modified enzymes were also examined in organic solvent. PEG-AOR showed enhanced (5-fold) activity for the reduction of benzyl viologen (BV) in aqueous solution, this could be in part due to the enhanced hydrophobic interaction between the PEG-AOR and substrate. Interestingly, the activity of PEG-AOR for the reduction of PEG-Fd is only ca. 17% of that of native AOR and Fd. It is suspected that the protein aggregation upon PEG-modification may be the cause for such activity loss. PEG-modified hydrogenase has a solubility of ~5 mg/ml in toluene. In the study of the catalysis of the solubilized hydrogenase in organic solvents, it was observed that addition of bulk water lead to obvious reduction sulfur dissolved in toluene. Based on this observation, a new reaction mechanism has been proposed:

$$^{2}H_2O + H_2 + S \text{ à } H_2S + {}^{2}OH^- + {}^{2}H^+$$

Planned Activities

Efforts are underway to expand the range of enzymes, contaminants and modification methods to translate the proposed unique approach to effective remediation processes. PCB is currently being investigated as are polyaromatic hydrocarbon. Fundamental studies of the catalytic behaviors of the solubilized hyperthermophilic enzymes will be continued, and it is expected that these studies would ultimately lead to the development of high performance enzymatic catalysts for use in organic solvents.

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New Strategies for Designing Inexpensive but Selective Bioadsorbants for Environmental Pollutants: Selection of Specific Ligands & Their Cell Surface Expression

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Research Objective

The broad, long term objective of the research plan is to develop exquisitely selective polypeptide metal chelators for the remediation of aqueous systems. A variety of polypeptide chelators will be developed and optimized ranging from antibodies to small peptides. Then, through unique molecular engineering approaches developed in our laboratories, the polypeptide chelators will be anchored directly on the surface of the cells that produce them. Thus, instead of using isolated biomolecules we will employ inexpensive genetically engineered whole cell adsorbents. Following a simple, easily scaleable treatment, the engineered cells can be used to manufacture an inexpensive, particulate adsorbent for metal removal.

Research Progress and Implications

We are currently in year two of a three year program. Work has been focused on preparing the molecular biology constructs needed to carry out the optimization of a metal complex binding antibody, and on the isolation of a metal binding peptide.

1) We have isolated genes for the V regions of the heavy and light chains for the Ru(bpy)3 specific monoclonal AC1106 (Shreder, K.S. Hariman, A. and Iverson, B.L., J. Am. Chem. Soc. 1996, 118, 3192-3201). This antibody binds Ru(bpy)3 derivatives with high affinity, and will serve as our generic metal-complex binding pocket.

2) A -((gly)3ser)4- linker was added between the heavy and light chain to complete the construction on a so-called single chain Fv (scFv). The scFv is the smallest functional unit of an antibody that retains full binding activity.
3) The scFv has been cloned into a pET25b(+) vector for soluble expression.
4) We have synthesized various metal complexes to be used for a thorough binding analysis and optimization studies of the scFv.
5) We have prepared milligram quantities of the AC1106 scFv and characterized the binding properties using a fluorescence enhancement assay. We have measured binding constants for the scFv binding to various Ru(bpy) derivatives.
6) We have cloned the scFv into our bacterial surface expression system in preparation for antibody engineering efforts. By using iterative rounds of randomization and selection via fluorescence activated cell sorting (FACS) the affinities for different metal ions will be evolved.
7) We have produced a sophisticated computer model of the scFv binding site to act as a guide for antibody engineering studies.
8) We have isolated Cu(II) and Ni(II) specific peptides using phage display technology. The isolated sequences contain histidine in the context of usually hydrophobic residues. These isolated sequences have improved physical properties compared to a simple polyhistidine peptide sequence.
9) We have initiated pilot studies to optimize the capture of metal complexes using the E. coli surface expressed scFv. The scFv reagent is prepared in "ready to use" form by simply growing a culture of cells. We are currently carrying out a systematic series of studies to find the best format for isolating metal complexes in a highly selective and efficient manner.
10) In advances related to the metal-binding work, we have been able to optimize further the efficiency of our bacterial surface expression/FACS selection system for isolating interesting new antibodies. Using the optimized protocols on an scFv that binds the heart glycoside digoxin, we were able to produce an improved scFv with subnanomolar affinity after a single round of selection (Daugherty, P., Chen, G., Iverson B. and Georgiou, G. Protein Eng. (1998) in press)! In addition, we have been able to combine multiple mutations isolated in different library screening studies. This new "supermutant" has an extremely high affinity, as the combined mutations conferred an additive increase in binding. These powerful new procedures will be employed in the upcoming metal-complex binding antibody evolution studies.
11) In another advance related to the metal-binding work, we have recently completed the saturation mutagenesis studies of an entire antibody binding pocket (Chen G., Mendez, P., Dubrawsky, I., Georgiou, G. and Iverson, B., manuscript submitted). In other words, all of the amino acid residues that contact the bound antigen were changed one at a time to every other possible amino acid. Each mutant, 190 in all, was analyzed quantitatively for binding activity. The extremely high throughput of mutants required by this study was accomplished through optimized techniques we have developed for the in vitro production and analysis of antibody mutants (Burks, E.A., Chen, G., Georgiou, G. and Iverson, B.L. Proc. Nat. Acad. Sci., USA , 1997, 94, 412-416). Analysis of the data produced the first comprehensive model of the functional roles played by each amino acid in the binding pocket. This model will be used to steer future antibody engineering efforts.

Planned Activities

The stage is now set to begin the final phase of our work.

1) We will begin the AC1106 scFv antibody optimization studies in which the affinity will be improved and the metal specificity will be modulated in different optimized scFv mutants. For these tasks we will utilize our E. coli surface display / FACS selection strategy (please see 10 above) as well as our systematic in vitro mutagenesis approach (please see 11 above). The binding properties of all the optimized antibodies will be characterized in detail. These studies will establish how well a generic metal complex specific antibody binding site can be optimized to bind a variety of different metal species with a high level of specificity.

2) We will continue to adjust the parameters of the pilot studies to use the metal specific, surface-expressed antibodies and peptides for purification. In particular, we will be analyzing various methods of attaching whole cells as well as isolated membranes to various solid supports. In this way, the loading capacity versus cost will be maximized.

Enzyme Engineering for Biodegradation of Chlorinated Organic Pollutants

Peter G. Schultz, Lawrence Berkeley National Laboratory

Research Objective

The generation of biological catalysts for the bioremediation of synthetic products will require in many cases powerful tools for modifying the catalytic and physical properties of natural enzymes. One approach to this problem involves the generation of selective catalysts by exploiting the large chemical diversity of the immune system to generate enzymelike catalytic antibodies. A second strategy involves the development of *in vitro* evolution methods to rapidly evolve protein catalysts with selected functions. We are attempting to combine both approaches to generate catalysts for the bioremediation of halogenated aromatics. Specifically, we are developing general selections and screens for identifying novel catalysts from large libraries of antibody mutants. These methodologies are being initially applied to a well-characterized esterolytic antibody 43C9, but if successful, will provide a general approach for evolving a wide range of catalysts for the dehalogenation of halocarbons.

Research Progress and Implications

Selections allow one to search large libraries of mutants for enhanced function. We are developing a general selection scheme that can be applied to any reaction that can be linked to the release of p-aminobenzoic acid, e.g., esterase, amidases, phosphodiesterases, glycosidases, etc. The shikimate pathway produces several small aromatic compounds, including *p*-aminobenzoic acid (PABA). *E. coli* with the chorismate synthase *aroC* mutation require an external source of PABA. A selection scheme based on the release of PABA is general, because PABA can be incorporated into a substrate molecule through either the carboxylic acid or the amine functional groups and with a variety of release mechanisms. As a model system for this selection scheme we chose to use the catalytic antibody 43C9, which hydrolyses the anilide bond in substrate **1**, which was elicited to hapten **2**. Changing the nitro group of the substrate to a carboxylic acid gives a substrate, **3**, which would release PABA upon hydrolysis of the anilide bond.

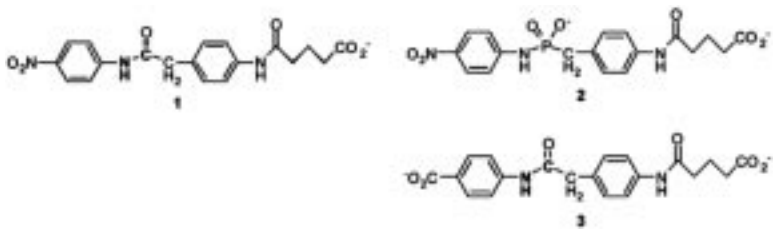

Figure 1

Using primers designed from a previously published sequence of 43C9, the antibody genes were reverse transcribed from murine messenger RNA and inserted into the expression vector, p4xH. The antibody expressed as a Fab fragment at a level of 1 mg per 1 L shake flask, and was catalytically active. The antibody was subcloned into another expression vector, pFH1, for inducible expression on solid media. Successful expression on minimal plates necessary for PABA selection was confirmed by ELISA. Additionally, HDU83, an *aroC* strain of *E. coli*, was tested with substrate **3** to verify the feasibility of the selection. Substrate **3** concentrations of 20 μM were required for colony growth, as compared to 20 nM of free PABA required for growth. This 1000 fold difference in minimum concentrations should provide an adequate margin for PABA-based selection. A library of 43C9 was created by DNA shuffling then ligated back into the expression vector. Two rounds of shuffling have been undertaken, the first simply introduced point mutations into the antibody genes, similar to error-prone PCR. The second (and subsequent) rounds introduce more mutations and also recombine existing mutations to produce more diversity. The library obtained from the second round of shuffling has been transformed into the HDU83 strain and plated onto minimal media containing 20μM of substrate **3**.

Planned Activities

We are also developing an automated system for screening libraries of mutants generated by DNA shuffling for enhanced activity. In order that the screen be generally applicable to a wide variety of reactions we are using mass spectrometry to directly detect conversion of substrate to product. Again the antibody 43C9 is being used as a model system. A substrate analogue has been synthesized which is linked to biotin via a positively-charged cleavable linkage

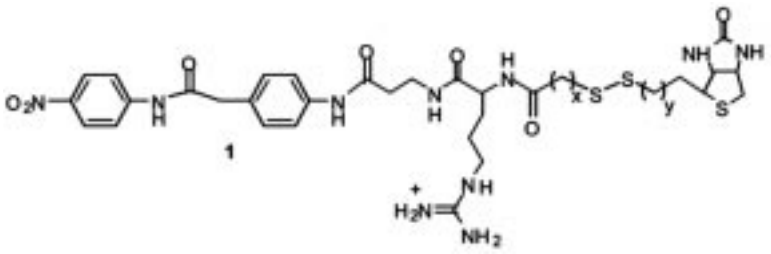

Figure 2

Growth of colonies in 100 μL cultures is followed by periplasmic lysis to release the antibody into the media. Substrate is added and after a desired reaction time streptavidin magnetic beads are then added followed by separation of reaction product and mass spectrometric analysis by MALDI. We are able to detect 25 pmoles of product. The above system is being automated by integrating a colony picker, robotic arm and 96 well culture plates and multiwell MALDI sample holders. We anticipate that the system under development will allow us to screen in an automated fashion 10,000 mutants/ day. The recombination process involved in shuffling should make it possible to rapidly combine additive mutations that lead to enhanced activity. Repetitive rounds of shuffling and screening should allow us to efficiently evolve a large range of catalytic properties.

Phase Equilibria Modification by Electric Fields

Costas Tsouris, Oak Ridge National Laboratory

Research Objective

The objective of this project is to use electric fields to favorably manipulate the thermodynamic and transport properties of mixtures so that higher separation efficiencies can be achieved. The main focus is to understand and quantify the influence of electric fields on vapor-liquid, liquid-liquid, and solid-liquid systems. It is expected that this program will lead to greater separation efficiency in a wide range of environmental treatment processes, including solvent extraction, sorption, distillation, and stripping. Such processes are widely used by DOE for treatment of wastes and sites contaminated with heavy metals, radionuclides, and organic solvents. Particular examples of applications of vapor-liquid-equilibria modification can be found in the separation of volatile organic compounds by either stripping or distillation. Improvements can also be made in liquid-liquid-extraction processes of TRU, Sr, Tc, and Cs by both thermodynamic and transport enhancements. Separations of metal ions by electro-sorption can be used to remove such metal ions as Cs, Sr, Co, Cr, Cd, Hg, and TRU.

Research Progress and Implications

Following is a summary of the work after 1 and 2/3 years of a 3-year project:

Vapor-Liquid Equilibria: Studies during the first year of this program showed that the separation factor for polar-polar and polar-nonpolar liquid mixtures was significantly increased by applying an electric field across the vapor-liquid interface (Blankenship et al., 1997). This work has been continued in the second year with focus on the geometry and distance of the electrodes, direction and strength of the electric field, and electrical properties of the components. Results consistently showed that, at low applied voltage (ca. 4-6 kV) there was no significant effect on the chemical composition of the two phases. At higher applied voltage, the separation factor of the mixture increased. It was found that the applied voltage is the key to vapor-liquid-equilibria modification, while the distance between the electrodes had little effect. These experimental results, coupled with numerical solutions of Maxwell's equations suggested that the mechanism of equilibria modification by electric fields is related to the charge density at the interface (Blankenship et al., 1998).

Liquid-Liquid Studies: Various binary and ternary liquid systems, including cyclohexane-water, cyclohexane-isopropanol-water, tributyl phosphate-water, and water-MIBK-acetic acid, have been employed in liquid-liquid-equilibria experiments. Unlike vapor-liquid systems, it is difficult to isolate an equilibrium effect of an electric field, since the application of a high voltage difference across a liquid-liquid interface causes significant electrohydrodynamic (EHD) flows. Such EHD flows have been extensively used in the past to enhance heat transfer in various processes. Experiments were conducted to further investigate the use of EHD flows in transport enhancement. It was found that electric fields cause simultaneous pumping, spraying, and mixing of fluids (Shin et al., 1997; Tsouris et al., 1998a). These phenomena were observed using various polar solvents including water, ethanol, propanol, 2-propanol, and butanol. Such phenomena may be employed to significantly enhance transport rates in solvent-extraction treatment processes.

Solid-Liquid Equilibria: It has been shown by other investigators that electro-sorption may lead to an efficient process for the removal of ions, including heavy metals and radionuclides, in which the sorbent is readily regenerated by removing the external electrical potential. The mechanism of electro-sorption is due to transport of ions from the aqueous solution to the solid-liquid interface and capture of the ions in the electric double layer formed at the surface of the electrodes. Electrochemical reactions may also occur at the electrodes. Equilibrium and kinetic experiments are conducted in order to better understand the mechanisms of electro-sorption and develop predictive models for

metal ion uptake by this phenomenon. In these experiments, the electrodes are made of carbon aerogel, a material composed of interconnected particles with microscopic interstitial pores (<50 nm), which is ideal for electro-sorption because of its high specific surface area (400 to 1100 m^2g^{-1}) and low electrical resistivity (< 40 mWcm). Preliminary experiments conducted with NaCl solutions showed that the conductivity of the solution decreased during applied electric field and increased after removing the field. These results indicate that the ions are captured in the electric double layer when the field is applied and are released back to solution when the field is removed.

Planned Activities

The following activities are planned for the remaining of the second and third year:

Gas-Liquid Systems: Studies will be focused on understanding the mechanisms of electric-field effects on vapor-liquid-equilibria. Raman spectroscopy will be used to study the interface with and without electric fields applied. Additional polar-polar and polar-nonpolar systems will be used in the experiments to determine the characteristics of suitable chemical systems, and testing will be conducted to determine approaches to effectively employ electric fields.

Liquid-Liquid Systems: Experiments will be conducted to quantify the effect of electric fields on phase equilibria of binary and ternary systems. Exploratory experiments will be undertaken in collaboration with B. A. Moyer (EMSP 55087) to determine the effect of applied electric fields on transport and equilibrium in solvent-extraction systems with advanced solvents developed in that program. In parallel, the work on EHD flows will be continued with the objective to better understand the underlying phenomena and develop devices that could be used for efficient separations.

Solid-Liquid Systems: A surface complexation model will be developed to predict equilibrium and kinetics of metal-ion uptake. This model will consider: (i) surface ionization, (ii) complexation of surface sites with ionic species, and (iii) the formation of an electrical double layer adjacent to the surface. The capabilities of this model are expected to include prediction of the effect of the various solution variables, such as pH, ionic strength, and metal ion concentration, as well as the effect of the electric field on the extent of electro-sorption. Experimental data will be obtained for model verification.

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An Investigation of Homogeneous and Heterogeneous Sonochemistry for Destruction of Hazardous Waste

Inez Hua, Purdue University

Research Objective

The primary objective of this research project is to acquire a deeper fundamental knowledge of acoustic cavitation and cavitation chemistry, and in doing so, to ascertain how ultrasonic irradiation can be more effectively applied to environmental problems. The primary objective will be accomplished by examining numerous aspects of sonochemical systems and acoustic cavitation. During the course of the project, the research group will investigate the significance of physical variables during sonolysis, sonochemical kinetics and reactive intermediates, and the behavior of heterogeneous (solid/liquid) systems. An additional component of the project includes utilizing various techniques to image cavitation bubble cloud development.

Research Progress and Implications

This report summarizes results after 2 years of a 3 year investigation. Four on-going projects will be described. The first project is the destruction of polychlorinated biphenyls at multiple ultrasonic frequencies. The second project is a comprehensive study of how ultrasonic frequency influences sonochemical reaction rates; in particular, hydrogen peroxide formation. Finally, the sonochemical destruction of the pesticides dichlorvos (at 500 kHz) and carbofuran (parallel-plate reactor) has been examined.

Polychlorinated Biphenyl Destruction

The sonolytic destruction of polychlorinated biphenyls (PCBs) has been performed. The ultrasonic frequency significantly impacted the reaction rate; a maximum pseudo – first order rate constant (0.5079 min^{-1}) was observed during sonication of 1.0 ppm 2-PCB in an Ar saturated solution at 358 kHz and a sound intensity of 5.5 W cm^{-2}. The three congeners exhibited variable rate constants: pseudo - first order rate constants for 0.87 ppm 2-PCB, 1 ppm 4-PCB, 20 ppb 2,4,5-PCB were 0.128 $min^{-1} \pm 0.0007$, 0.097 $min^{-1} \pm 0.001$, and 0.157 $min^{-1} \pm 0.003$ respectively, during irradiation at 20 kHz. The reaction rates were proportional to power intensity, and inversely correlated to initial concentration. Chlorine recovery as chloride ion was 78%, 76% and 69% for 2-PCB, 4-PCB, and 2,4,5-PCB respectively. Scavenging of hydroxyl radical by bicarbonate decreased the reaction rate by 53% at a bicarbonate concentration of 50 mM, indicating the important role of free-radical attack during sonochemical destruction of PCBs. Spin-trapping and electron spin resonance (ESR) indicated that phenyl radical is a reactive intermediate during the transformation of PCBs (2-PCB and 4-PCB) and biphenyl was detected with gas-chromatography/mass spectroscopy (GC/MS) analysis of sonicated solutions.

Sonolysis of Dichlorvos

The sonochemical destruction of dichlorvos was carried out at a sound frequency of 500 kHz with an acoustic output power ranging from 86 to 161 Watts. Power and sparge gas were important determinants of sonochemical destruction rates. The effect of acoustic power on the degradation rate was investigated for an Ar-saturated solution. The pseudo-first order rate constants for dichlorvos disappearance are 0.0184±0.0014, 0.0258±0.002, and 0.0374±0.0023 min^{-1} for 86, 124, and 161 Watts respectively. The variation of the rate constants due to sparge gas (Argon, Oxygen, and Ar/O_2 mixture) was also examined. The pseudo-first order rate constants for dichlorvos disappearance, during sonication at 161 Watts, were 0.0319±0.0035, 0.0374±0.0023, and 0.0792±0.005 min^{-1} for Oxygen, Argon, and

Argon/Oxygen mixture, respectively. Total Organic Carbon (TOC) analysis is used to determine the extent of complete mineralization (formation of carbon dioxide from organic carbon) during the destruction of dichlorvos. After 50 minutes of sonication at 161 Watts, the TOC concentration decreased by 20% for both Argon and Oxygen sparge and by 27% for the Argon/Oxygen mixture.

Sonolysis of Carbofuran

The purpose of this particular study was to examine a larger volume, higher power flow-through reactor. Carbofuran, a carbamate pesticide, has been found in the groundwater of at least seven states, and the United States Environmental Protection Agency (U.S. E.P.A) has established a maximum contaminant level (MCL) of 0.04 mg/L. The sonochemical degradation of carbofuran in a parallel plate near-field acoustical processor (NAP) was carried out with simultaneous irradiation at 16 and 20 kHz, and a total power of 1800 W. The degradation rate constants increase with increasing power density and decreasing initial (bulk) concentration. The nature of the cavitating gas (Ar or Ar/O_2) also determined how quickly carbofuran was destroyed during sonication. Experiments were conducted with varying power-to-volume ratios (1.65, 4.22 and 5.55 W mL^{-1}), initial concentrations of either 25 μM or 130 μM, and a dissolved gas of either 100% Ar or 80:20 (v/v) Ar/O_2 . The maximum rate constant, k= 0.0749 $\pm$ 0.0008 min^{-1} is observed during sonication at 5.55 W mL^{-1} , at an initial concentration of 25 μM, and with Ar/O_2 as the saturating gas. Nitrate and nitrite were quantified and 86% of the organic nitrogen in carbofuran is recovered as NO_x. Tracer studies using the conservative tracer sodium chloride (NaCl)were performed to characterize the hydrodynamic behavior of the NAP reactor.

Hydrogen Peroxide Production

Hydrogen peroxide (H_2O_2) production rates during acoustic cavitation in Ar-saturated water have been investigated over a range of frequencies and power intensities. Results from tests conducted at four ultrasonic frequencies (205, 358, 618, and 1071 kHz) and seven power intensities at each of the four frequencies (1.0, 2.0, 3.1, 4.1, 5.1, 7.7 and 8.2 W cm^{-2}) show a direct correlation between zero-order H_2O_2 production and power intensity. Moreover, the H_2O_2 production rate at 358 kHz tended to be greater than those at 205, 618 and 1071 kHz, for a given intensity. At 205 kHz, a maximum production rate is observed at 5.1 W cm^{-2} ; however, the production rates increase with intensity (up until 8.0 W cm^{-2}) at each of the other three frequencies. The H_2O_2 formation rate for each frequency-intensity combination was determined over the course of 45 minutes of sonication; and each combination was tested in triplicate. The results of this study show that of the four frequencies tested, 358 kHz is the most efficient in terms of H_2O_2 production; an optimal efficiency of 0.3 $nmoleJ^{-1}$ occurs at 358 kHz and 4.1 W cm^{-2}.

Planned Activities

Further investigations of chemical kinetics and transformation products will be carried out during the final phase of the project. In order to truly understand sonochemical effects, the behavior of the individual bubbles and the bubble clouds must be more finely resolved. Physical characterization of cavitation bubble clouds will also be performed. Thus, a more fundamental link will be established between bulk, observable parameters and sonochemistry, via the physics and hydrodynamics of the cavitating cloud.

Other Access To Information

Professor Hua's Web URL is: **http://CE.www.ecn.purdue.edu/CE/Fac_Staff/FACULTY/hua**

Phytoremediation of Ionic and Methyl Mercury Pollution

Richard B. Meagher, University of Georgia

Research Objective

The long-term objective of our research is to manipulate single-gene traits into plants, enabling them to process heavy metals and remediate heavy-metal pollution by resistance, sequestration, removal, and management of these contaminants. We are focused on mercury pollution as a case study of this plant genetic engineering approach. The working hypothesis behind this proposal was that "transgenic plants expressing both the bacterial organo mercury lyase (merB) and the mercuric ion reductase gene (merA) will: A) remove the mercury from polluted sites and B) prevent methyl mercury from entering the food chain." The results from our research are so positive that the technology will undoubtedly be applied in the very near future to cleaning large mercury contaminates sites. Many such sites were not remediable previously due to the excessive costs and the negative environmental impact of conventional mechanical-chemical technologies.

Research Progress and Implications

At the time this grant was awarded 20 months ago, we had successfully engineered a small model plant, Arabidopsis thaliana, to use a highly modified bacterial mercuric ion reductase gene, merA9, to detoxify ionic mercury (Hg(II)), reducing it to much less toxic and volatile metallic Hg(0) (Rugh et al., 1996). Seeds from these plants germinate, grow, and set seed at normal growth rates on levels of Hg(II) that are lethal to normal plants. In assays on transgenic seedlings suspended in a solution of Hg(II), 10 ng of Hg(0) was evolved per min per mg wet weight of plant tissue. At that time, we had no information on expression of merA in any other plant species, nor had we tested merB in any plant. However, the results were so startlingly positive and well received that they clearly presaged a paradigm shift in the field of environmental remediation. We have broken our new results in to two sections following from our hypothesis.

A. Removing the mercury from polluted sites— The small size of Arabidopsis plants prevented us from carrying out more complex physiological studies and field tests, so transgenic tobacco, Liriodendron tulipifera (yellow poplar), and Brassica napus (rape seed) plant lines expressing merA derivatives were constructed. In each case expression of merA leads to striking resistance to Hg(II) relative to control plants.

   When grown on highly mercury-contaminated soil, merA transgenic Arabidopsis and tobacco shoot samples accumulated very low levels of mercury, while controls if they grow at all, accumulated substantial levels. We interpret this experiment as follows: expression of the MerA protein catalyzes Hg(0) volatilization and loss from the system and prevents Hg(II) from becoming strongly bound to plant tissues. This is an important result, because it suggests that the MerA-expressing plants will be safer for herbivores to consume than native plants growing at a contaminated site.

   Using transgenic tobacco, a number of experiments have examined the mechanisms of mercury processing by these plants. For example, we demonstrated that when merA9 tobacco plants are grown in hydroponic media with 1 ppm Hg(II) (i.e., 1000 μg total in Hg(II) in 1 liter), they volatilize 80% of the mercury from the system in a week, whereas the control plants have little impact. All the Hg(II) is bound to roots of both control and merA9 plants in the first 24 hrs, but only the transgenic plants efficiently eliminated mercury from the roots over the next few days. As in the above experiments with soil only small amounts of mercury were found in stems or leaves of the merA9 tobacco plants. These data suggest that MerA-expressing transgenic plants: 1) can be used immediately to process industrial waste streams contaminated

with mercury, and 2) work efficiently even at very low levels of Hg(II) (i.e., the EPA limit for water is typically about 1 ppm).

Next we focused on determining if metallic Hg(0) vapor transpired up through the vascular system and out of leaves, as are H_2O vapor, O_2, and CO_2. We also wanted to test models in which the plants were "engineered" to trap mercury instead of volatilizing it. In one set of experiments we demonstrated that transgenic yellow poplar plantlets efficiently volatilized Hg(0) into the air from solid agar growth. These results were quite suggestive of a transpiration mechanism. In a second set of experiments, we grafted all combinations of merA and wild-type tobacco tops and roots together and grew them hydroponically for one week with Hg(II) in their media. Again merA transgenic tissues accumulate little mercury in roots, stems, or leaves relative to control tissues. However, as predicted by the transpiration model, wild-type tops grafted over merA root system accumulate substantially more mercury than any other sample. This is presumably because Hg(0) vapor produced by the merA root system is transpired to the wild-type tops where it is reoxidized to Hg(II) by endogenous catalases and peroxidases and trapped as Hg(II). This suggests the likelihood of a transpiration mechanism and demonstrates the feasibility of phytoextracting mercury from soil and water and trapping it above ground tissues for later removal.

Many of the largest mercury contaminated sites with the most serious environmental impact due to the production of methyl mercury (below) are aquatic or marine ecosystems. Aquatic and marine grasses engineered to express MerA would be the most suitable for complete remediation of such environments. New merA gene constructs are being made for monocot expression using a variety of promoters.

B. Preventing methyl mercury from entering the food chain— Endogenous bacteria at most aquatic and marine sties produce an organic form of mercury, called methyl mercury, which is the most serious threat to the environment. Methyl mercury is biomagnified up the food chain, poses an immediate threat to wildlife and human populations, and is the most common source of mercury poisoning. Gram-negative bacteria living in these environments often encode an organo mercury lyase, MerB, which protonolyzes the carbon mercury bond to produce the less toxic Hg(II). The activity of a partially engineered merB gene was confirmed in E. coli and transformed into Arabidopsis. Seeds from the merB plants germinate and seedlings grow on 0.1-2 μM (0.02-0.4 ppm) phenyl mercury acetate (PMA) or methyl mercury chloride, while the wild-type germinants died. Similar results were obtained with merB transgenic tobacco. When merA9 and merB are combined genetically into the same Arabidopsis plants they are resistant to even higher levels of methyl mercury (10 μM). Our work strongly suggests that native macrophytes (e.g., trees, shrubs, grasses) engineered to express merBpe derivatives could be used to clean methyl mercury from polluted sites and prevent it from entering the food chain.

Planned Activities

The next year focuses on preparing merA/merB tobacco and rice lines, and testing their ability to break down methyl mercury and transpire Hg(0).

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Molecular Genetics of Metal Detoxification: Prospects for Phytoremediation

David W. Ow, United States Department of Agriculture

Research Objective

We seek to define the genes involved in heavy metal tolerance and sequestration. Two complementary approaches were taken: 1) clone and characterize the genes that complement cadmium hypersensitive mutants of fission yeast, specifically those responsible for production of metal-binding complexes, and 2) isolate genes that can confer cadmium hypertolerance to wild type strains of fission yeast.

Research Progress and Implications

This work summarizes present status of a 3 year project beginning September 1, 1996.

Mutant analysis: Mutant JS282 hypoproduces phytochelatins: A 7 kb genomic DNA fragment complements the mutant. However, the genomic clone on a multicopy vector causes hypersensitivity to cadmium or selenium in wild type strains. Two cDNAs have been isolated and sequenced. A 0.75 kb cDNA is probably not full length, but shows 70% sequence similarity to a S. cerevisiae gene suspected to encode a membrane protein. Expression of this cDNA does not confer hypersensitivity to Cd or Se in wild type strains. A second cDNA of 1.8 kb was isolated, but it lacks sequence similarity to proteins in the data base. This 1.8 kb cDNA could confer Cd and Se hypersensitivity to wild type cells.

Mutant JS246 also hypoproduces phytochelatins: A genomic clone that restores Cd tolerance has been isolated. Interestingly, wild type strains harboring the genomic clone on a multicopy plasmid are hypertolerant to cadmium. Three cDNAs corresponding to this genomic clone have been sequenced. cDNA#1 is about 1.3 kb and shows sequence similarity with a bacterial oxidative stress protein; cDNA#2 is about 1 kb and shows similarity to a S. cerevisiae gene of unknown function; cDNA#3 is only 0.4 kb and does not show similarity to genes in the data base.

Mutant JS237 fails to accumulate the sulfide-containing phytochelatin-cadmium complex. This mutant was found to have a mRNA splicing defect in a gene homologous to the human Wiskott-Aldrich Syndrome protein (WASP). The human disease symptom is associated with defects in cytoskeletal organization. Likewise, mutant JS237 exhibits aberrant arrangement of polymerized actin. The fission yeast WASP has been found to co-localize with cortical actin and to interact with actin associated proteins. The genomic clone complements the defect associated with the polymerized

actin organization, but did not fully restore Cd tolerance. Hence, we suspected that another gene is encoded by the genomic fragment. This led to the identification of an upstream mRNA that overlaps the WASP coding region. This mRNA encodes a P-type ATPase. Most members of this family are associated with cation transport, however, this clone shows strongest sequence similarity to aminophospholipid translocases. We tested for but failed to observe aminophospholipid translocase activity. Thus, the possibility of it being a cation transporter remains open. Constructs have been made to express this protein for production of polyclonal antibodies.

S. pombe cDNAs that confer hypertolerance to cadmium: A cDNA expression library was made in a fission yeast vector such that selection for clones that confer high level tolerance can be made. Some 40 clones were isolated and sequenced. These cDNAs reveal a variety of genes, including one that encodes a Class I (animal-type) metallothionein protein. Hence, fission yeast also has a metallothionein which is not used in response to metal stress, but when overproduced through artificial means, can nonetheless confer tolerance. Other genes encode enzymes in glutathione biosynthesis and proteins that are involved in calcium binding or oxidative stress. Some proteins show no sequence similarity to known proteins.

Plant metallothioneins that confer cadmium hypertolerance to fission yeast: A cDNA library was made from the mRNA of Brassica juncea (Indian Mustard), a metal-hyperaccumulating plant. When introduced into fission yeast, cadmium hypertolerant clones were isolated and found to encode Class II metallothionein genes. 3 cDNAs were found which encoded distinct members of the Class II metallothionein (MT) family. A smaller cDNA (369 bp) encoding a Class II type 1 MT (45 amino acids) and two larger cDNAs (492 and 535 bp) encoding a Class II type 2 MTs (80 amino acids each) were sequenced.

Metal binding peptides in Brassica juncea: Studies were initiated to define the distinct roles of phytochelatins and metallothioneins in metal hyperaccumulation in B. juncea. B. juncea seedlings were treated with Cd and/or Cu and were harvested for analysis of the accumulation of phytochelatin peptides and metallothionein mRNA. Treatment of B. juncea seedlings with 12.5, 50 and 200 mM Cd resulted in increasing levels of phytochelatins (PCs) predominantly from n=2 to 4 (n is the number of Glu-Cys units). Cu treatment caused only an increase of PC accumulation at 12.5 and 50 mM Cu. At the 200 mM Cu treatment, an inhibition of PC(n=2) and PC(n=4) occurred with a concomitant appearance of an as yet unidentified compound. Based upon the detection method using DTNB, it can only be concluded that this compound contains a reduced sulfhydryl group.

Planned Activities

Molecular genetic characterization of the mutants is progressing from the stages of gene isolation and characterization to the stages of determining protein localization and function. Localization of the protein products will involve generating antibodies against the proteins. Functional analysis, especially of the cDNAs that confer hypertolerance, will involve gene disruption studies to reveal the loss-of-function phenotype. For physiological characterization of metal binding complexes in B. juncea, mRNA probes from the metallothionein genes will determine the relationship between their expression and the appearance of phytochelatin peptides. In addition, amino acid composition will be determined for the undefined metal-binding species observed during the HPLC analysis of phytochelatins.

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Characterization of a New Family of Metal Transport Proteins

Mary Lou Guerinot, Dartmouth College

David Eide, University of Missouri-Columbia

Research Objective

Soils at many DOE sites are contaminated with metals and radionuclides. Such soils obviously pose a risk to human and animal health. Unlike organic wastes which can be metabolized, metals are immutable and cannot be degraded into harmless constituents. Phytoremediation, the use of plants to remove toxic materials from soil and water, may prove to be an environmentally friendly and cost effective solution for cleaning up metal-contaminated sites. The success of phytoremediation will rely on the availability of plants that absorb, translocate, and tolerate the contaminating metals. However, before we can engineer such plants, we need more basic information on how plants acquire metals. An important long term goal of our research program is to understand how metals such as zinc, cadmium and copper are transported across membranes. Our research is focused on a new family of metal transporters which we have identified through combined studies in the yeast *Saccharomyces cerevisiae* and in the model plant *Arabidopsis thaliana*. We have identified a family of 19 presumptive metal transport genes in a variety of organisms including yeast, trypanosomes, plants, nematodes, and humans. This family, which we have designated the "*ZIP*" genes, provides a rich source of material with which to undertake studies on metal transport in eukaryotes. The project has three main objectives:

Objective 1: Determine the sub-cellular location of the ZIP proteins in *Arabidopsis*.

Objective 2: Carry out a structure/function analysis of the proteins encoded by the *ZIP* gene family to identify regions of the protein responsible for substrate specificity and affinity.

Objective 3: Engineer plants to overexpress and underexpress members of the *ZIP* gene family and analyze these transgenic plants for alterations in metal accumulation. We now know that manipulation of transporter levels will also require an understanding of post-transcriptional control of *ZIP* gene expression.

Research Progress and Implications

We are currently in year one of a three-year project. We are concentrating on Arabidopsis ZIP family members that variously transport iron, zinc and manganese when expressed in yeast. In plants, three of the family members, *ZIP1*, *ZIP3* and *ZIP4*, are up-regulated by zinc deficiency and one, *IRT1*, is up-regulated by iron deficiency. We have constructed ten site-directed mutations in IRT1 by changing conserved histidine, aspartic acid and glutamic acid residues to alanine residues. While most of the mutations abolish both iron and zinc uptake activity, three mutations, E103A, H197A and E305A, have little or no zinc uptake activity but retain wild type levels of iron uptake activity. In addition, three chimeric proteins between IRT1 and either ZIP1 or ZIP3 have been constructed. However, all of the constructs assayed to date have little or no iron or zinc activity. Transgenic plants engineered to either overexpress or underexpress a particular transporter gene are allowing us to test the relative importance of each transporter in maintaining ion balance. This year, we have focused on analyzing lines carrying *IRT1* sense constructs. In wild-type Arabidopsis plants, *IRT1* mRNA is only expressed in iron-deficient roots, whereas transgenic plants carrying a CaMV 35S:: *IRT1* construct show expression of *IRT1* mRNA in roots and shoots under both iron-deficient and iron-sufficient conditions. However, IRT1 protein is only detected in the roots of iron-deficient transgenic plants. Metal analysis

of transgenic plants showed that several lines accumulate iron, zinc and manganese as compared to wildtype; these lines have higher levels of IRT1 protein than wildtype under permissive (iron-deficient) conditions, indicating a correlation between IRT1 protein level and metal accumulation. In addition, lines that have elevated levels of IRT1 protein show an enhanced sensitivity to cadmium under iron-deficient conditions and yeast expressing IRT1 also show an enhanced sensitivity to cadmium.

Planned Activities

During the next year, we will begin analysis of additional transgenic plant constructs, including *IRT1* antisense plants, and sense and antisense constructs for *ZIP1*, *ZIP2* and *ZIP3*. We will continue our structure-function studies, focusing on the random mutagenesis approach. We will also continue to prepare family member specific antibodies for use in localization studies. At the present time, we have antibodies directed against IRT1 and against ZIP3.

Other Access To Information

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Heavy Metal Pumps in Plants

Jeffrey F. Harper, Scripps Research Institute

Research Objective

The purpose of the proposed DOE research is to determine the function of AMA1, a novel heavy metal pump identified in a model plant system, Arabidopsis. Heavy metal pumps belong to a superfamily of P-type ATPases which include the plasma membrane Na/K-ATPase in animals and the plasma membrane H^+-ATPase in plants and fungi. Heavy metal pumps have been implicated in heavy metal resistance (e.g., cadmium) and regulation of essential micronutrients (e.g., copper). Although several heavy metal pumps have now been identified in plants, their isoform specific functions have not been investigated. Our results suggest that AMA1 is a molydenum uptake pump. We are exploring the possibility to engineer the ion specificity of these pumps to take up other heavy metals from the soil.

Research Progress and Implications

This report summarizes work after 2 years of a 3 year project. As of June 1998, we have identified and cloned a gene encoding a heavy metal pump from Arabidopsis, called AMA1 (Arabidopsis Heavy Metal ATPase-isoform 1). Sequence analysis indicates that AMA1 encodes a P-type ATPase with a predicted molecular weight of 102 kDa. Eight putative transmembrane domains are predicted with a “CPC” motif, characteristic of heavy metal P-type ATPases, located in the middle of transmembrane 4. AMA1p is distinquished from other heavy metal pumps by a unique 26kD

C-terminal domain with multiple metal binding motifs rich in histidine and cystein, with cysteins commonly found as CC pairs.

AMA1p is localized to the plasma membrane, as indicated by aqueous two phase partioning and immunodetection of the pump using two different polyclonal antibodies raised against the N- and C-terminal domains. Western blot analysis of root and shoot tissues indicates that AMA1p is primarily expressed in roots and flowers.

To genetically investigate the biological function of AMA1, we identified a plant line containing a T-DNA disrupted allel, ama1-1. The ama1-1 knock-out was identified by screening a collection of Agrobacteria-transformed Arabidopsis using PCR reactions. A T-DNA was found inserted in the N-terminal coding region, at a site immediately before the first transmembrane domain. This research identifies the first mutation of a heavy metal pump in plants.

In comparison to a wild-type parent, homozygous ama1-1 knock out plants were healthy and showed normal development under standard growth conditions. However, metal analysis indicated that ama1-1 plants had a reduced accumulation of one metal, molybdenum. Heavy metal concentrations were measured using Ion Conductive Plasma-Optical Emission Spectrometry (ICP-OES). In 4 week old plants grown on 0.5x Murashige and Skoog media, molybdenum accumulation was reduced to 25% (2.3 ppm) in knock-out plants, while normal metal concentrations were measured for calcium, cobalt, copper, iron, magnesium, manganese, and zinc.

Our results are consistent with the hypothesis that AMA1p functions as a molybdenum uptake pump in plant roots. Although molybdenum is an essential metal for enzymes involved in nitrogen and sulfur metabolism, little is known about how this metal is transported within cells. This research provides the first evidence for a P-type ATPase involved in molybdenum transport.

A continued effort is recommended to engineer P-type ATPases to transport heavy metals for bioremidiation purposes.

Planned Activities

A long term goal is to engineer new ion specificities into P-type ATPases. This would allow the design of new pumps to transport other essential and toxic heavy metals, such as manganese, cadmium, chromium, copper or gold. As a first step we need to better understand the structural basis for ion selectivity. To produce enzymes for biochemical and structural analysis we have been developing protocols for functional expression of P-type ATPases in yeast. Our short term goal is to evaluate the functional activity of AMA1 when expressed in yeast.

Our research on P-type ATPases extends to other pumps which translocate calcium, sodium, protons, and manganese. A comparative study of these different pumps should help us understand how a common enzymatic mechanism has evolved to specifically transport so many different ions.

Specific objectives for the next year:

1. Confirm that the ama1-1 knock out plant has a disruption of a heavy metal uptake system. The approach is to measure uptake rates of molybdenum and other heavy metals. Metals will be detected using radioactive labels or with ICP-OES.
2. Determine if AMA1p alters heavy metal homeostasis when expressed in yeast. The approach is to express AMA1p in wild type yeast and a mutant harboring a disruption of both endogenous heavy metal pumps. Metals will be detected using ICP-OES.
3. Consider strategies to use yeast to establish a genetic selection system to identify mutant pumps with altered ion specificities.

Molecular Dissection of the Cellular Mechanisms Involved in Nickel Hyperaccumulation in Plants

David Salt, Northern Arizona University

Research Objective

Phytoremediation, the use of plants for environmental cleanup of pollutants, including toxic metals, holds the potential to allow the economic restoration of heavy metal and radionuclide contaminated sites. A number of terrestrial plants are known to naturally accumulate high levels of metals in their shoots (1-2 % dry weight), and these plants have been termed metal-hyperaccumulators. Clearly, the genetic traits that determine metal-hyperaccumulation offers the potential for the development of practical phytoremediation processes. Our long-term objective is to rationally design and generate plants ideally suited for phytoremediation using this unique genetic material.

Initially, our strategy will focus on isolating and characterizing the key genetic information needed for expression of the metal-hyperaccumulation phenotype. Recently, histidine has been shown to play a major role in Ni hyperaccumulation. Based on this information we propose to investigate, at the molecular level, the role of histidine biosynthesis in Ni hyperaccumulation in *Thlaspi goesingense*, a Ni hyperaccumulator species

Research Progress and Implications

We have been successful at cloning three key genes involved in histidine biosynthesis in plants, THG1, THD1 and THB1, encoding for ATP phosphoribosyltransferase (ATP PRT), imidazoleglycerol phosphate dehydratase (IGPD), and histidinol dehydrogenase (HD) (Fig. 1), respectively. The genes were cloned by functional complementation of *Escherichia coli* mutants lacking the gene of interest. Complementation of the *E. coli* mutant CGSC 4289 - which lacks a functional ATP PRT gene - by the

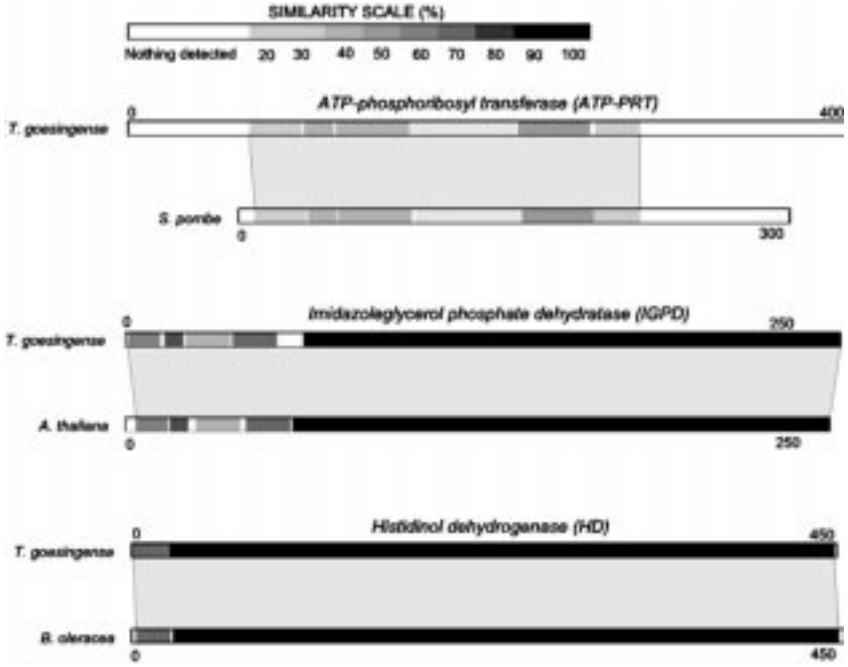

Figure 1. Amino acid aliments of histidine biosynthetic genes cloned from the Ni hyperaccumulator T. goesingense with the same genes from other species.

T. goesingense THG1 gene is shown in Figure 2 as an example. This type of functional complementation provides strong evidence for the identify of the cloned genes.

We have isolated mRNA from *T. goesingense* exposed to Ni and we are now in the process of using THG1, THB1 and THD1 as probes to study the transcriptional regulation of these genes by nickel, using Northern analysis. All three *T. goesingense* genes (THG1, THB1, THD1) have also been engineered into an *E. coli* expression vectors for expression and purification of the recombinant proteins. We have recently been successful at expressing THG1 in *E. coli* and we are now in the process of purifying the recombinant His-tagged ATP PRT (Fig. 3). From the SDS-PAGE gel, the plant ATP PRT has a molecular weight of approximately 48 kd, which compares well with that of other ATP PRT's from different sources. Once purified, the activity of ATP PRT will be studied for allosteric regulation by nickel and hisitdine. The ATP PRT enzyme from *E. coli* is strongly inhibited by its product, phosphoribosyl ATP, and our preliminary studies suggest this is also true for our plant enzyme.

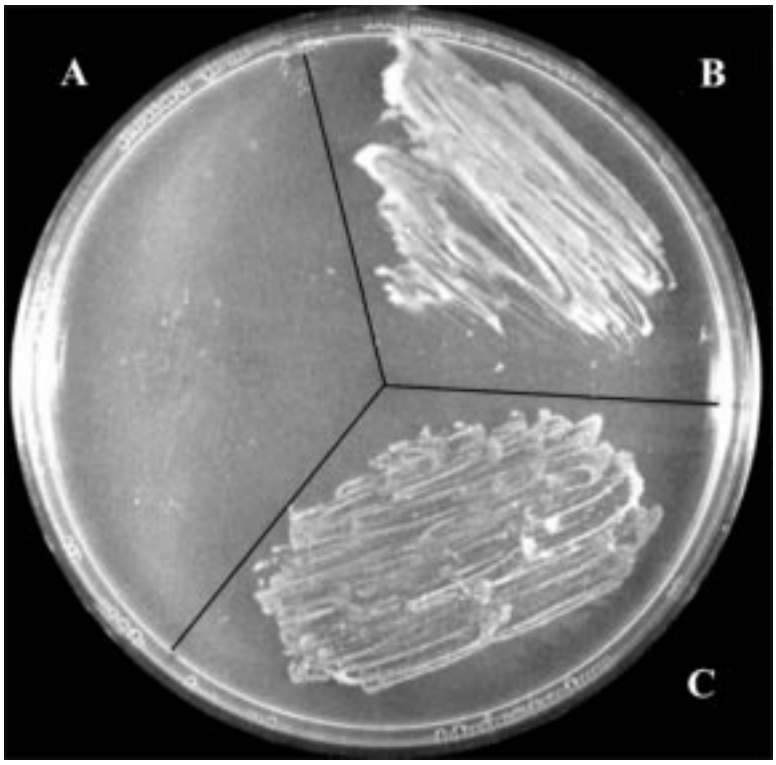

Figure 2. **Functional complementation of a HisG$^-$ mutant E. coli (CGSC 4289), unable to grow in the absence of histidine, with the Thlaspi THG1 gene. Minimal medium lacking histidine;** A**, HisG$^-$ transformed with pTrip-THD1;** B**, HisG$^-$ transformed with pTrip-THG1;** C**, Wild-type TOP10F' with p Trip-THG1. Similar results have also been with THD1 and THB1.**

To efficiently assay the *T. goesingense* ATP PRT activity, it will be necessary to remove the product of the reaction by adding the product degrading next enzyme in the sequence, phosphoribosy ATP pyrophosphatase. This enzyme is not available commercially, therefore, we are in the process of cloning it by PCR from *E. coli* (Fig. 4). Plasmid DNA containing the *E. coli* histidine operon has been obtained from Dr. D.J. Savic and Dr. C.B. Bruni. Using primers specific to the His I gene, encoding phosphoribosy ATP pyrophosphatase, we have successfully amplified a 680 bp DNA fragment which should correspond to the His I gene (Fig. 4). We will clone this fragment and check its identity by functional complementation of a His I$^-$ *E. coli* mutant. Once the identify of the fragment as His I (encoding phosphoribosy ATP pyrophosphatase) is confirmed, we will engineer it into an *E. coli* expression vector, purify the recombinant protein for use in the ATP PRT enzyme activity assay.

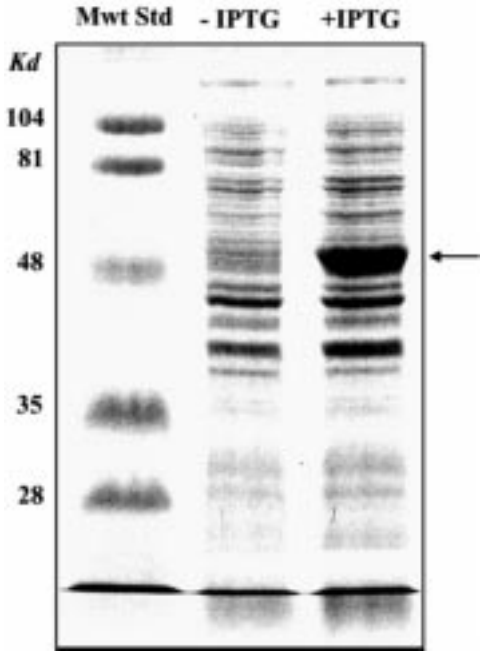

Figure 3. **SDS-PAGE gel of total protein from E. coli transformed with the pET-30 expression vector containing the THG1 gene. Cells were induced at 22°C with 0.4 mM IPTG for 3 h, resulting in expression of the THG1 gene and accumulation of the gene product (see arrow).**

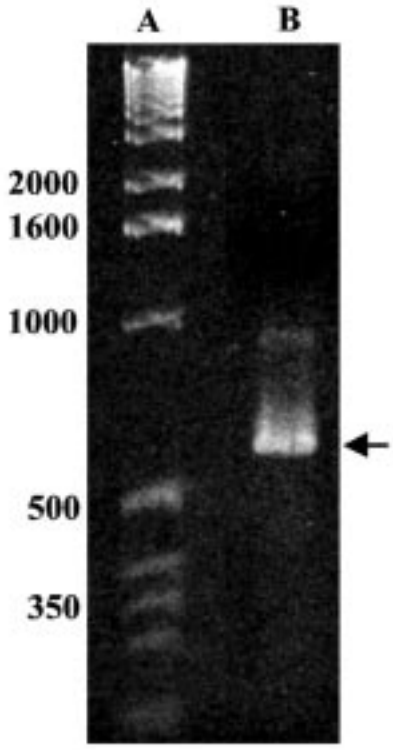

Figure 4. **PCR products from amplification of E. coli His I gene.** A. **DNA ladder;** B**, PCR reaction containing expected 680 bp fragment (see arrow)**

Planned Activities

If Northern analysis of mRNA shows significant regulation of THG1, THD1 and THB1 by Ni, we will raise antibodies against the recombinant proteins and measure the level of the proteins in plants after exposure to Ni. We will also perform *in-situ* hybridizations using the THG1, THD1 and THB1 genes as probes to determine the tissue localization of Ni regulation of these genes. We will also make transgenic *Arabidopsis thaliana* over expressing THG1, THD1 and THB1 to determine if increased production of histidine is sufficient to allow increased accumulation of Ni by plants.

Molecular Characterization of a Novel Heavy Metal Uptake Transporter from Higher Plants & its Potential for Use in Phytoremediation

Julian I. Schroeder, University of California at San Diego

Research Objective

Soils and waters contaminated with high levels of heavy metals such as Cadmium, Lead and Copper are detrimental to human and environmental health. Many human disorders have been attributed to environmental contamination by heavy metals. Removal of heavy metals from highly contaminated sites is therefore a very costly but necessary process that is currently being pursued. Recent research in several laboratories indicates that uptake of heavy metals into plants via the root system may provide a cost-effective approach for decontamination of certain heavy metal-laden soils and waters. Several mechanisms have been identified, which allow detoxification in the cytosol and vacuoles of plants. However, the molecular biological mechanisms by which heavy metals are transported from soils across the plasma membrane into roots have remained largely unknown. In recent research, our laboratory has cloned a cation uptake transporter cDNA from plants. Yeast cells expressing this cDNA show enhanced uptake of calcium and cadmium. The proposed research is testing the transport of toxic and nutrient metals by the encoded protein.

Research Progress and Implications

Molecular and functional characterization of a novel low-affinity cation transporter (LCT1) in higher plants. [Daniel P. Schachtman[1], Raman Kumar[1], Julian I. Schroeder[2] and Ellen L. Marsh[1]. [1]Department of Botany, University of Adelaide, Adelaide, SA 5005 Australia; and [2]Department of Biology and Center for Molecular Genetics, University of California at San Diego, La Jolla, CA 92093-0116]

An initial report, describing the cloning of LCT1 was published by Schachtman et al., 1997, Proc. Natl. Acad. Sci. USA 94:11079-11084. The transport of cations across membranes in higher plants plays an essential role in many physiological processes including mineral nutrition, cell expansion, and the transduction of environmental signals. In higher plants, the coordinated expression of transport mechanisms is essential for specialized cellular processes and for adaptation to variable environmental conditions. To understand the molecular basis of cation transport in plant roots, a Triticum aestivum cDNA library was used to complement a yeast mutant deficient in potassium (K+) uptake. Two

genes were cloned that complemented the mutant: HKT1 and a novel cDNA described in (Schachtman et al., 1997) encoding a cation transporter, LCT1 (low-affinity cation transporter). Analysis of the secondary structure of LCT1 suggests that the protein contains 8-10 putative trans-membrane helices and a hydrophilic amino terminus containing sequences enriched in Pro, Ser, Thr, and Glu (PEST). The transporter activity was assayed using radioactive isotopes in yeast cells expressing the cDNA. LCT1 mediated low-affinity uptake of the cations Rb^+ and Na^+, and possibly allowed Ca^{2+} but not Zn^{2+} uptake. LCT1 is expressed in low abundance in wheat roots and leaves. The precise functional role of this cation transporter is not known, although the competitive inhibition of cation uptake by Ca^{2+} has parallels to whole plant and molecular studies that have shown the important role of Ca^{2+} in reducing Na^+ uptake and ameliorating Na^+ toxicity. The structure of this higher plant ion transport protein is unqiue and contains PEST sequences. This study was published by: Schachtman et al., 1997, Proc. Natl. Acad. Sci. USA 94:11079-11084.

The plant transporter LCT1 mediates the uptake of calcium and cadmium in yeast. [Stephan Clemens[1], Danuta M. Antosiewicz[1], John M. Ward[2], Daniel P. Schachtman[3] and Julian I. Schroeder[1]. [1]Department of Biology and Center for Molecular Genetics, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0116, USA; [2]Institut für Botanik, University of Tübingen, Auf der Morgenstelle 1, D-72076 Tübingen, Germany; and [3]Department of Botany, University of Adelaide, Adelaide, SA 5005 Australia.]

Non-essential metal ions such as cadmium are most likely taken up by plants via nutrient transporters. To identify possible pathways for Cd^{2+} uptake we tested putative plant cation transporters for Cd^{2+} uptake activity by expressing cDNAs in S. cerevisiae and found that expression of one clone, LCT1 (Schachtman et al., 1997, Proc. Natl. Acad. Sci. USA 94:11079-11084), renders the growth of yeast more cadmium-sensitive. Ion flux assays showed that Cd^{2+} sensitivity is correlated with an increase in Cd^{2+} uptake. LCT1-dependent Cd^{2+} uptake is saturable, lies in the high-affinity range (apparent KM for Cd^{2+} ˜33 μM) and is sensitive to block by La^{3+} and Ca^{2+}. Growth assays demonstrated a sensitivity of LCT1-expressing yeast cells to extracellular millimolar Ca^{2+} concentrations. LCT1-dependent increase in Ca^{2+} uptake correlated with the observed phenotype. Furthermore, LCT1 complements the disruption of a non-LCT1-homologous yeast gene encoding a membrane Ca^{2+} influx system We conclude that LCT1 mediates the uptake of Ca^{2+} and Cd^{2+} across the plasma membrane of yeast cells.

Schachtman, D.P., R. Kumar, J.I. Schroeder and E.L. Marsh (1997) Molecular and functional characterization of a novel low-affinity cation transporter (LCT1) in higher plants. Proc. Natl. Acad. Sci. USA 94:11079-11084.

Planned Activities

Because uptake of heavy metals into plant cells is toxic and detoxification mechanisms are essential, we are pursuing research to characterize genes that enhance Cd^{2+} resistance.

Other Access To Information

Clemens, S., D.M. Antosiewicz, J.M. Ward, D.P. Schachtman and J.I. Schroeder (Submitted) The plant transporter LCT1 mediates the uptake of calcium and cadmium in yeast.

Using Trees to Remediate Groundwaters Contaminated with Chlorinated Hydrocarbons

Stuart E. Strand, University of Washington

Milton P. Gordon, University of Washington

Research Objective

Industrial practices in the past have resulted in contamination of groundwater with chlorinated hydrocarbons (CHCs) at many DOE sites, such as Hanford and Savannah River. Such contamination is a major problem because existing groundwater remediation technologies are expensive and difficult. An inexpensive method for groundwater remediation is greatly needed. Trees could be used to remediate CHC polluted groundwater at minimal cost (phytoremediation). Before phytoremediation can be extensively applied, we must determine the range of compounds that are attacked, the effects of metabolic products on the plants and the environment, and the effect of transpiration and concentration of CHC on uptake and metabolism.

We will test the ability of hybrid poplar to take up and transform the chlorinated methanes, ethanes and ethylenes. The rate of uptake and transformation by poplar of TCE as a function of concentration in the soil, transpiration rate and illumination level will be determined. Methods will be developed to permit rapid testing of plants from contaminated sites for species able to oxidize and sequester chlorinated compounds. We will identify the nature of the bound residues of TCE metabolism in poplar. We will identify the mechanisms involved in CHC oxidation in poplar and use genetic manipulations to enhance that activity. We will introduce the genes for mammalian cytochrome P-450-IIE1, known to oxidize light CHCs such as TCE to attempt to increase the CHC metabolism capacity of poplar.

The results of this research will place phytoremediation of CHCs on a firm scientific footing, allowing a rational assessment of its application to groundwater contamination.

Research Progress and Implications

This report summarizes the results of the first 1.5 years of work on a three-year project.

Laboratory and field tests with poplar in tissue culture, bioreactors, and field sites have shown that, unlike bacteria, plants are able to carry out complete degradation of fully chlorinated alkanes and alkenes to carbon dioxide and chloride. Carbon dioxide was produced as a product of the degradation of trichloroethylene (TCE), carbon tetrachloride (CT), and perchloroethylene (PCE) when axenic tissue cultures of poplar cells were exposed to radiolabeled compounds. The apparent degradation of PCE and CT, fully chlorinated hydrocarbons, in these aerobic plants is remarkable when contrasted to the lack of comparable aerobic degradation by bacteria. Oxidized metabolites, such as trichloroethanol and di- and trichloroacetic acid, were detected in cell cultures exposed to TCE, suggesting the involvement of cytochrome P-450s or other monooxygenase activities. Mass balance experiments with small poplar plants in laboratory reactors showed that significant TCE and CT was volatilized from leaves, while a similar fraction of radiolabeled carbon from these chlorinated solvents was retained in the plant tissue.

Early in the project we discovered that large poplar growing in full sun took up TCE and CT without significant solvent transpiration. Pilot scale experiments in the field were carried out using cells containing approximately 12 m3 soil with an underlying send layer through which an artificially contaminated groundwater flowed. Hybrid poplar were planted in the cells (15 trees per cell). TCE or CT was added to the influent of the cells at concentrations ranging from one to 100 mg/L, but generally averaging 15 mg/L. Control cells consisted of poplar planted cells with no solvent exposure and cells with TCE or CT exposure but no vegetation. Mass removal of TCE and CT from the

groundwater in the cells exceeded 95 percent. Laboratory tests of soil from the cells showed that there was no enhancement of CT or TCE degradation in the rhizosphere soils. Transpiration of TCE and CT by the hybrid poplar at the test site was measured by two methods: long-path open FTIR and by bagging leaves and trapping solvent vapors. By both methods air emissions of the chlorinated solvents accounted for less than 6 percent of the total removal. All of the total chloride introduced to one of the planted cell as TCE during the 1997 season was recovered as chloride ion in the soil, suggesting that dechlorination of TCE was complete. Although some chlorinated metabolites (e.g., chloroacetic acids and trichloroethanol) were founded plant tissues, there was no significant increase in total organic chlorides in the tissue of trees exposed to solvent compared to unexposed controls. We conclude that poplar can destructively remove TCE and CT without harmful air emissions or accumulation of a hazardous solid waste.

The metabolism of TCE in poplars has been investigated in detail using axenic cultures of poplar cells or small plants grown in the greenhouse. The following metabolites were found: CO_2, trichloroethanol, chloral, trichloroacetaldehyde, and di- and trichloroacetic acid. In addition, carbon from the TCE was detected in the purified lignin fraction.

Many of the products observed in the plant experiments are identical to those which arise from the action of cytochrome P450 on TCE. We, accordingly, are carrying out the transformation of poplars with several heme containing cofactors and enzymes in attempts to increase the oxidizing capacity of the plant tissue. We prepared plasmids, containing mammalian cytochrome P450 2EI, cytochrome b5, and cytochrome oxidoreductase. This complex is stated to be responsible for the catabolism of CHCs in the mammalian liver. In addition, a plasmid containing mammalian beta-chain of hemoglobin was prepared. All of the plasmids were incorporated into the bacterium, Agrobacterium tumefaciens, and used to transform Nicotiana tabacum, Xanthi n.c. (the guinea pig of the plant world) and young shoots of Populus trichocarpa x P. deltoides. We now have nine tobacco plants growing with the enzyme complex containing the full cytochrome P450 2EI complex. We also have a number of tobacco plants with a tetrameric form of beta-chain hemoglobin. The poplar plants are still too small to be tested for foreign genes.

Planned Activities

In the next 1.5 years the following studies will be undertaken. Planned experiments in the field include tests of the of the TCE and CT degradative abilities of willow, various poplar, and black locust and of the ability of poplar to degrade PCE. Experiments to determine the biochemical mechanism of TCE and CT degradation in plants using axenic tissue culture are continuing. Metabolic studies with the transgenic plants, especially degradation of TCE, will be undertaken in the near future when the plants are sufficiently large. We are also in the process of preparing axenic suspension cultures of the transformed tissues for use in these studies.

Plant Rhizosphere Effects on Metal Mobilization and Transport

Teresa W.-M. Fan, University of California at Davis

Research Objective

Introduction and Objectives

Information on the mechanism of how plants mobilize, uptake, and metabolize metal ions is very limited. Especially deficient is the understanding of these processes involving pollutant metal ions and interactions among these ions. Based on our current knowledge regarding nutrient ions, it is

clear that elucidation of rhizospheric processes such as exudation of organic ligands by plant roots and plant metabolism/adaptation involving these biogenic chelators is critically important. A mechanistic insight into these processes will advance knowledge in microbe-plant host interactions and how metal ions are mobilized, immobilized, and sequestered by these interactions. This, in turn, is essential to applications such as phytobioremediation and microbioremediation of metal ion pollution.

Root exudation also serves many other important rhizosphere functions including energy supply for microbial degradation of organic pollutants, structuring of microbial community, and the formation of soil humic materials which are considered to be a major sink for both organic and inorganic pollutants. How root exudates function is critically dependent on the chemical nature of exudate components. Therefore, a comprehensive characterization of all major exudate components, regardless of their chemical class, should facilitate the development and implementation of bioremediation for both organic and inorganic pollutants.

Therefore, the objectives of this project are:

(1) To obtain a comprehensive composition of major organic components in plant root exudates as a function of different metal ions;
(2) To examine plant metabolic response(s) to these metal ion treatments, with emphasis on biosynthetic pathways of organic ligands; and
(3) To investigate the effect(s) of soil microbial (e.g. mycorrhizae) association on (1) and (2).

Research Progress and Implications

In the 1st year of the project, we utilized multi-nuclear, two-dimensional NMR and GC-MS techniques to determine all of the major components in barley root exudates under Fe sufficient and deficient conditions. Both structural and quantitative information was obtained directly from crude root exudates without sample fractionation, which enables detection of unknown and unexpected compounds. This greatly faciliates chemical characterization of root exudates and ensures that no major components escape detection.

We found that a number of organic ligands were excreted by barley roots including the phytosiderophore mugineic acids (2ı-deoxymugineic acid, mugineic acid, and 3-epi-hydroxymugineic acid) and a number of amino and organic acids. The amount of mugineic acids excreted was correlated positively with the extent of Fe deficiency, with 3-epi-hydroxymugineic acid being the most prominent component. The increase in mugineic acid excretion was accompanied by an elevation in the tissue content of Cu, Zn, and Mn. The total Fe chelating capacity was also measured using the ferrozine assay and compared with the production of the mugineic acids. We were surprised to find that the mugineic acids may account for only part of the Fe chelating capacity, especially under mild and moderately Fe deficient conditions. Lactate, alanine, g-aminobutyrate (GAB), malate, and glycinebetaine (GB) collectively may contribute to a significant fraction of the Fe chelating capacity. In light of the known stimulatory effect of alanine and citrate on metal availability to algae (Campell, 1995), the function of these low molecular weight metabolites as vehicles for Fe or metal uptake in general require further investigation. This work was published in Analytical Biochemistry 251, 57-68 (1997).

We then proceeded to apply the above approach to investigate the interaction of elevated cadmium (Cd) with Fe deficiency in gramineous plants. We have completed one each series of cadmium (Cd) treatments of barley, wheat, and rice seedlings under Fe sufficient and deficient conditions. The purpose of these experiments was to examine the role of mugineic acids in Cd uptake and the effect of Cd on the chemistry of root exudates. We found that the chemical composition of root exudates differed substantially among these three plants. The wheat root exudates were dominated by 2ı-deoxymugineic acid and a polyol component, the barley root exudates were abundant in 3-epi-hydroxymugineic acid and several amino and organic acids with the polyol a minor component, while the major components of rice root exudates included lactate, acetate, Gly, and glyceraldehyde-3-phosphate.

In the cases of barley and wheat, the excretion of mugineic acids was stimulated by Fe deficiency but suppressed by the Cd treatments, particularly under Fe deficient conditions. For barley, the increase

in tissue Cd content was positively correlated with the amino acids (Ala, Gly, GAB, Ser, Thr, Asp, Glu) and glycinebetaine. In comparison, the excretion of the polyol component by wheat roots was greatly enhanced by Cd uptake, and that on a per gram basis, wheat roots and shoots sequestered much more Cd than those of barley. These results indicate that the phytosiderophore mugineic acids may not be important in Cd uptake into gramineous plants and that the polyol component may play a significant role in Cd mobilization and sequestration. We presented these findings at the annual meeting of the Society for Environmental Toxicology and Chemistry-Europe at Bordeaux, France, and two manuscripts are being prepared.

As for rice, detailed analysis of exudate and tissue components is still ongoing. A preliminary analysis indicated that the excretion of glyceraldehyde3-phosphate may be enhanced by the Cd treatments.

We have also developed methods to probe the dynamic relationships between metal ions, siderophores, and humic substances. Using pyrolysis-GCMS and multidimensional NMR, we found that the bacterial siderophore, desferrioxamine, is capable of extensive association with humic materials. This is significant because all current models and concepts assume exchange of metal ions between competing, but otherwise non-interacting, ligand sites. This work shows that the two interacting ligands significantly reduces the formation of the siderophore-Cd ion complex. This work is being published in The Analyst, 1998, in press.

In addition to exudate measurement and experiments, we are developing a convenient analysis of sulfhydryl-rich chelator components in Cd-treated plant tissues. This method is based on the derivatization of sulfhydryl (SH) groups in peptides and proteins by bromobimane, followed by separation and quantification using gel electrophoresis. A preliminary analysis of Cd-treated rice tissues incidated that the production of several small SH-rich peptides (most likely phytochelatins) were greatly enhanced by the Cd treatments.

In summary, it is clear that the composition of root exudates varies substantially among plant species and that different exudate components may be involved in Cd uptake into plant tissues. If understood, the relationship among plant species, exudate chemistry, and metal ion mobility may be utilized to engineer the mobilization or immobilization of a spectrum of metal ions in contaminated soils.

Planned Activities

In the next four months, we are conducting ^{15}N and ^{13}C tracer studies on wheat seedlings in solution cultures to investigate the biosynthesis of excreted ligands such as the polyol component and intracelluar ligands as a funciton of Cd treatments. Such studies should help reveal the metabolic flux and pathways for these ligands, which should facilitate the understanding of the molecular genetics involving metal mobilization and sequestration.

In the next year, we also plan to conduct a similar series of experiments with Al treatments to elucidate the organic ligands involved in Al mobilization/immobilization and tolerance.

To more rapidly gain an understanding of how exudate chemistry effects pollutant ion uptake and how this process interacts with the uptake of other plant mineral ions, we are implementing an energy dispersive X-ray fluorescence (ED-XRF)-based method for convenient quantification of multi-elements ranging from 23Na to lanthanides. The method is non-destructive and applicable to a wide range of sample matrices (e.g. plant powders, soils, aqueous solution) with no sample digestion required. The XRF instrument has been installed recently and a preliminary survey indicates that all macro and micro plant nutrient elements can be simultaneously acquired along with pollutant elements including Al, Cd, Pb, Ag, Sr, As, Se, Ba, and Sn present at ppm level in plant tissues.

Furthermore, we are developing a pyrolysis-GC/MS based microanalysis for exudate ligands that are involved in Fe and Cd mobilization. Our preliminary results indicate that the hydroxamate type siderophores such as desferrioxamine can be analyzed directly in soil matrix. Such direct soil analysis of biogenic ligands and XRF analysis of multi-elements in soils and plant tissues will be employed in the next year to investigate the interaction between exudate chemistry and metal ion sequestration in soil-grown plant systems.

Construction of Bending Magnet Beamline at the APS for Environmental Studies

Edward A. Stern, University of Washington

Research Objective

Design and construction of a bending magnet beamline at the Advanced Photon Source (APS) by the Pacific Northwest Consortium-Collaborative Access Team (PNC-CAT). The beamline will be optimized for x-ray absorption spectroscopy (XAS) studies with a major focus on environmental issues. The beamline will share the experimental facilities under development at the neighboring undulator based insertion device beamline. It will utilize these facilities for XAS of both bulk and surface samples, with spatial and elemental imaging, on toxic and radioactive samples. It will help meet the rapidly growing need for the application of these techniques to environmental problems.

Research Progress and Implications

This report summarizes progress after 1-1/2 years of a 3-year project. The original scope of the project was to build a basic bending magnet beamline. Since the start of the project we have obtained addition funding from DOE-BES for the PNC-CAT activities. This has allowed us to expand the scope of the original proposed bending magnet beamline. Additional items now planned include a full sized experimental enclosure separate from the first optical enclosure (FOE), a white beam vertically collimating/focusing mirror providing improved flux and focusing, and enhanced experimental capabilities. Construction of the FOE and new experimental enclosure are complete along with full sector utilities, and the FOE is currently undergoing validation for its radiation integrity. The major beamline components are still being funded by the original EMSP project, and their status is described below.

The preliminary design of the beamline has been completed and accepted by the APS. The final design report is nearly complete and will soon be submitted to the APS for approval. This has allowed us to begin component procurement. For the initial phase of operation we require a monochromator, beam stops and shutters, and beam transport. The main shutter/beam stop is an APS design. It has been ordered and will be delivered in the summer of 1998. Procurement of the major monochromator components has begun. The monochromator will be very similar to the monochromator currently undergoing testing on our insertion device beamline, and we are awaiting the outcome of these tests before the final design of the crystal mounts. We expect the monochromator to be complete in early 1999. At this time limited testing with monochromatic beam can start in the FOE. The beam transport components are mainly standard UHV pumps and valves, and their procurement will begin with the approval of the final design report. A filter assembly originally planned for the ID line will be modified to act as a white beam slit system to complete the first stage of beamline development. The basic beamline should be operational in the spring of 1999, approximately 6 months ahead of the original schedule. This is a result of the additional DOE funding which accelerated the enclosure construction, and allowed us to concentrate the EMSP funds on beamline components.

The beamline will utilize experimental equipment being developed as part of the larger PNC-CAT effort. Microfocusing optics based on tapered capillaries and Kirkpatrick-Baez mirrors are under devlopment on the ID line. The capillary optics have been used to produce images with 0.5 micron resolution. A prototype K-B mirror has been completed, and will be tested soon. It will produce a focus of about 20 micron, and can also be used in conjunction with short tapered capillaries to improve their performance. Once perfected we plan to build versions of these optimized for the characteristics of the BM line. Recently we have also commissioned a portable UHV-MBE system which can be used for surface-XAFS, x-ray reflectivity, and standing wave measurements.

Finally, procedures for handling sensitive and radioactive materials are being developed in consultation with the APS and the ANL chemistry department. The chemistry department is funded by DOE to provide support facilities for the use of radioactive samples at the APS. We plan to carry out the first measurements using sensitive materials on the ID line in Aug 1998.

Planned Activities

As outlined above the primary planned activity is to bring the bending magnet beamline to full operation. Some important milestone dates follow:

June 1998 complete FOE radiation validation, complete shutter/beam stop assembly, submit final design report
February 1999 complete monochromator assembly
April 1999 first mono. Beam in FOE
June 1999 install beam transport to experimental enclosure
August 1999 bring mono. beam into the experimental enclosure for shielding tests
September 1999 commission sagittal crystal bender for horizontal focusing

This will complete the EMSP project, and the line will be capable of a full range of experiments. In FY2000, the additional DOE funding will be used to add a white beam focusing/collimating mirror to increase the focusing capabilities and flux.

Other Access To Information

A publication which summarizes our tapered capillary and micro-XAFS activities is:

S.M. Heald, D.L. Brewe, B. Barg, K.H. Kim, F.C. Brown, and E.A. Stern, "Micro-XAS using Tapered Capillaries Concentrating Optics", J. Phys. IV colloque C2, 297 (1997).

Microsensors for In-Situ Chemical, Physical, and Radiological Characterization of Mixed Waste

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Research Objective

A widespread need exists for portable, real-time, in-situ chemical, physical, and radiological sensors for characterization of mixed wastes, groundwater, contaminated solids, and process streams. None of the currently available technologies offer a clear path to the development of sensors that are miniature, cost-effective, selective, highly sensitive with a wide dynamic range, and have the ability to work in air or liquid while providing chemical, physical, and radiological information. The objective

of this research program is to conduct the fundamental research necessary to develop microcantilever-based micromechanical sensors for in-situ characterization of groundwater, sediments, and mixed wastes. Chemical selectivity will be achieved by coupling surface modification chemistry with molecular recognition agents. Physical measurements of adsorption (absorption) induced deflection (bending) and resonance frequency variation of microcantilevers can be achieved with extreme precision resulting in ppb-ppt sensitivity.

Research Progress and Implications

Good progress has been made in the first nine months of this project. Progress has been made in three focus areas: radiation detection, detection of heavy metals in water, modification of microcantilever surfaces for chemical selectivity, and pH measurement. We have achieved some interesting and significant results in these four areas. We have developed a novel sensor concept for radiation detection based on variation in resonance transients induced by alpha particles. This concept can also be extended to the detection of other heavy charged particles. Although these experiments were conducted in air, they can be used in liquids also. Heavy metal in water (lead) was detected using electrochemical microcantilevers. In these experiments, a silicon microcantilever with one surface coated with a thin gold film was used as a working electrode in a three electrode electrochemical cell. When the potential of the cantilever was changed with respect to a reference electrode, lead was electrodeposited on the cantilever surface. Since the deposition occured only on one surface, the cantilever bent due to differential stress on the surface. Microcantilever based sensors can yield additional information that other electrochemical detection methods cannot produce. Electrochemical systems produce signals only when charged particles cross the soild-liquid interface while microcantilevers produce bending signals when the charge particles are on the surface. Thirdly, progress has also been made in modification of microcantilever surfaces for chemical speciation. For example, chloro- and alkoxysilanes bind to surface hydroxyls on metals and oxide surfaces. The degree of coverage and cross-linking through alkoxy sidechains can be controlled by reaction conditions and surface preparation. Another approach for chemical selectivity that is routinely used in mass sensors is the application of polymeric film forming materials to sensor surfaces. The chemical interactions that allow selectivity are provided by the polymer subunits. Cantilevers modified with chemically specific coatings show adsorption-induced bending. Progress has also made in the area of microcantilever pH measurement. Microcantilevers with a coating that changes surface charge density as a function of the pH of the solution undergo bending if the opposite surface is made inert. We have obtained a near Nerstian behavior for microcantilever pH sensors made out of silicon and silicon nitride.

Planned Activities

Planned activities for rest of the year include developing surface coatings for chemical speciation and new techniques for radiation detection. Surface coatings that can maintain stable operation under corrosive conditions will be pursued. Experiments using many systems will be conducted for furthering the understanding of adsorption-induced forces on real-surfaces. All the experiments will be conducted under solution. Other approaches for radiation detection using microcantilevers other than transient techniques will be tested. Second year goals include detection of ppb-levels of Hg, Pb, and Cr in water and developing chemically selective ionophores of Cs and Tc and evaluating their selectivity in presence of K, and Na.

Development of an In-Situ Microsensor for the Measurements of Chromium and Uranium in Groundwater at DOE Sites

Joseph Wang, New Mexico State University

Research Objective

The goal of this research is to develop novel electrochemical sensors for in-situ environmental monitoring of trace uranium and chromium. Such innovative remote/submersible and micromachined stripping-based devices will greatly enhance the detection of trace metals in a field setting, and should revolutionize the way such contaminants are being monitored.

Research Progress and Implications

This report summarizes our activity over the first 1.5 years of a 3-year project. This effort has led to the replacement of conventional stripping electrochemical protocols and systems with new innovative strategies for field monitoring of trace uranium and chromium, based on remotely deployable submersible sensors and micromachined hand-held total stripping analyzers. Eventually, these developments will allow to move the measurement of these metals to the field and to perform them more rapidly, reliably and inexpensively.

Improved Stripping Procedures for U and Cr

Traditionally, Cr and U have been measured separately using the adsorptive accumulation of their complexes with DTPA and propyl gallate (PG), respectively. To facilitate their on-site detection, we have developed new adsorptive stripping protocols that allow the simultaneous and rapid detection of Cr and U down to low ppb concentrations. One such new scheme involves the use of a mixed ligand (DTPA/PG) solution that allows simultaneous trace measurements in a single run (1). Numerous experimental parameters were optimized to assure that the attractive performance of the individual single- element protocols are not compromised. Simultaneous measurements in groundwater samples were documented. Alternately, we employed a single but more 'universal' ligand (cupferron) for the simultaneous monitoring of Cr and U (2). Under optimal conditions, competition of these metals for the ligand and coadsoprtion effects were minimized, and different concentrations of the mixture components can be tolerated.

Micromachined Stripping Analyzer

A major goal and focus of this project has been the development of a miniaturized stripping analytical system, produced by micromachining technology. Such new micromachined stripping analyzers - integrating all the sample manipulations steps(including complex formation) with the adsorptive stripping measurement - will require minimal amounts of sample and reagent and will result in faster and cheaper operations.

The newly designed microsystem uses an arrangement of functional modules, stacked on top of each other (to form a miniaturized flow system), including the sample and ligand/reagent reservoirs, two micro/piezo pumps, mixer, reaction coil, a silicon-based electrochemical detector and a micropotentiostat. The detector has a flow-through channel with an array of iridium microelectrodes, along with reference and counter electrodes, prepared by a photolithographic process. The size of the modules is 24x24 mm^2. The complete pocket-size microanalyzer has been assembled and delivered. Preliminary results are very encouraging, with both trace (ppb) Cr and U yielding well-defined signals. Yet, we still face various technical challenges, such as limited stability of the microfabricated reference

electrode or of the array of iridium microelectrodes, and an insufficient pumping capability. These limitations are currently being addressed, along with fundamental studies on the scaling-down effects.

Submersible Probe for In-Situ Detection of Trace Cr and U

Remotely-deployable submersible sensors, capable of monitoring Cr and U both in time and location, are advantageous in various situations. Such in-situ monitoring capability offers a rapid return of the chemical information and avoids errors associated with sample collection and storage. We have thus developed a new remotely deployable flow-probe, based on the coupling of the internal ligand delivery and microdialysis sampling for the in-situ detection of Cr and U (3). Such a renewable-reagent remote adsorptive stripping sensor relies on the continuous delivery of the ligand, its complexation reaction with the metal collected by the semi-permeable sampling tube, and transport of the complex to the downstream electrode compartment. Besides the in-situ detection, the microdialysis sampling offers minimization of surfactant effects and extended linear range (compared to conventional adsorptive stripping measurements) due to its filtration and dilution actions. In-situ sensing of metal speciation is also being investigated.

Conclusions

Our work over the first half of the project has resulted in novel and powerful protocols for in-situ electrochemical analysis of trace Cr and U. Such developments offer great promise for performing metal testing more rapidly, easily, and inexpensively in a field setting. These advances bring significant changes to the monitoring of Cr and U, and of toxic metals, in general.

References

1. J. Wang et al, Anal. Chim. Acta 354(1997)275.
2. J. Wang et al, Electroanalysis 9(1997)1247.
3. J. Wang et al, Anal. Chem. 69(1997)2640.

Planned Activities

Future work will aim at addressing problems encountered in the micromachining of the miniaturized stripping analyzer (Summer 1998), integration and miniaturization of the remote flow probe (Fall 1998), charaterization and optimization of both in-situ detection schemes (Fall 1998 and Winter 1999),their extensive in-situ testing (Spring and Summer 1999) and final reporting (Fall 1999). Based on our accomplishments so far, we are very optimistic that these studies will lead to powerful tools for in-situ detection of Cr and U.Fabrication on the micromachined system will focus on improving the stability of the reference electrode and the adhesion of the insulator surrounding the iridium ones. Attention will be given also to the integration of a micropump, compatible with the entire microsystem. Efforts with the remote metal sensor will include integration of the electronic control circuits and the micropump with the sensing element in a single submersible unit. A new software will be developed to control the entire sequence of events of both operations, as well as their data processing. Both systems will undergo extensive evaluation and testing.

In the long run, we will combine the two schemes by developing a fully submersible remotely deployed miniaturized stripping analyzer (in a a ‘lab-on-a cable’ configuration), and will combine this powerful metal detection capability with continuous monitoring of other priority pollutants.

Other Access To Information

Anal. Chem. 69(1997)1657-1661.

Novel Analytical Techniques Based on an Enhanced Electron Attachment Process

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Research Objective

Sensitive and selective detection of dense non-aqueous liquids (DNAPL), volatile organic compounds (VOC), and other organics, such as polychlorinated biphenyls (PCB), is an area of importance.

Current analytical methods for the detection of these compounds rely on their propensity to form negative ions. However, for compounds with smaller electron capture cross sections, including PCBs with few chlorine atoms and non-chlorinated VOCs, these methods are considerably less sensitive.

The objective of our research program is to develop novel analytical techniques that can be expected to be applicable for a wide variety of molecules with high sensitivity. These are based on the recently discovered enhanced negative ion formation process involving electron attachment to highly-excited states of molecules. We are using two approaches to produce the precursor highly-excited states; one is laser excitation, and the other is discharge based.

Research Progress and Implications

Within the past year and a half we have achieved the following:

1. Laser-Based Approach

   The basic physics involved in the dissociative electron attachment to laser-excited molecules was investigated:

   -L. A. Pinnaduwage and Y. Zhu, "Long-time stability of superexcited high-Rydberg molecular states", Chem. Phys. Lett. 277, 147 (1997).
   -L. A. Pinnaduwage and Y. Zhu, "High-Rydberg fragment formation via core dissociation of superexcited Rydberg molecules", J. Chem. Phys. 108, 6633 (1998).
   -L. A. Pinnaduwage and K. Nagesha, Phys. Rev. Lett. (A comment, submitted 1998).
   -Y. Zhu and L. A. Pinnaduwage, "Long-Time Stability of Superexcited High Rydberg Molecular States", 50th Annual Gaseous Electronics Conference, Madison, Wisconsin, October 6-9, 1997.

   It was illustrated the analytically useful negative ions can be produced by this method in benzene and toluene, which is not possible using conventional negative ion technique.

   -L. A. Pinnaduwage, K. Nagesha, Y. Zhu, M. V. Buchanan, and G. B. Hurst, Anal. Chem.(Submitted, 1998).

2. Discharge-Based Approach

   It was illustrated that molecules can be efficiently excited via excitation transfer from metastable states of rare gases produced in a glow discharge, and that electron attachment to those highly-excited molecules leads to abundant negative ion formation:

   -L. A. Pinnaduwage, D. L. McCorkle, and W. Ding, "Enhanced electron attachment to highly excited molecules using a plasma mixing scheme", Appl. Phys. Lett. 71, 3634 (1997).
   -W. Ding, D. L. McCorkle, and L. A. Pinnaduwage, "Enhanced formation of negative ions by electron attachment to highly-excited molecules in a flowing afterglow plasma", J. Appl. Phys. (Submitted , 1998)

   This is a novel method for producing characteristic negative ions. In these pioneering experiments, we have produced H^- and O^- ions from CH_4 and O_2 to illustrate the concept.

Planned Activities

1. Our studies on negative ion formation in laser-irradiated molecules have shown that it is indeed an extremely efficient process. However, the negative ion formation in those experiments is limited by the limited number of electrons produced by laser photoionization. We plan to provide additional electrons by using an external electron gun. The electron gun needed for these studies is being designed. (Anticipated time period: 1998-1999).
2. Using the new electron gun, mass spectrometric studies will be conducted on a variety of volatile organics of relevance to the DOE's environmental restoration program to characterize ion fragment formation. (Anticipated time period: 1999-2002).
3. We will evaluate the analytical capabilities of this novel method, such as the sensitivity (detection limits) and the selectivity (effects of interferences) (Anticipated time period: 2000-).
4. A novel pulsed discharge technique will be tested for the enhanced production of characteristic negative ions.(Anticipated time period: 1998-1999). If successful, this could be developed to a novel electron capture detector. (Anticipated time period: 1999-2000).
5. A mass spectrometer can be incorporated to the plasma apparatus to conduct mass spectrometric studies of negative ions, and then to study characteristic anion formation. (Anticipated time period: 1999-2002).

Fundamental Studies of the Removal of Contaminants from Ground and Waste Waters via Reduction by Zero-Valent Metals

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C. Amrhein, University of California at Riverside

Research Objective

Contaminated groundwater and surface waters are a problem throughout the United States and the world. In many instances, the types of contamination can be directly attributed to man's actions. For instance, the burial of wastes, casual disposal of solvents in unlined pits, and the development of irrigated agriculture have all contributed to groundwater and surface water contamination. The kinds of contaminants include chlorinated solvents and toxic trace elements that are soluble and mobile in soils and aquifers. Oxyanions of selenium, chromium, uranium, arsenic, and chlorine (as perchlorate) are frequently found as contaminants on many DOE sites. In addition, the careless disposal of cleaning solvents, such as carbon tetrachloride and trichloroethylene, has further contaminated many groundwaters at these sites. Oxyanions of selenium, nitrogen, arsenic, vanadium, uranium, chromium, and molybdenum are contaminants in agricultural areas of the Western U.S.

The management of these waters requires treatment to remove the contaminants before reuse or surface water disposal. In one instance in the Central Valley of California, the discharge of selenate-contaminated shallow groundwater to a wildlife refuge caused catastrophic bird deaths and deformities of embryos.

A potential remediation method for many of these oxyanions and chlorinated-solvents is to react the contaminated water with zero-valent iron. In this reaction, the iron serves as both an electron

source and as a catalyst. Elemental iron is already being used on an experimental basis. Both in-situ reactive barriers and above-ground reactors are being developed for this purpose. However, the design and operation of these treatment systems requires a detailed process-level understanding of the interactions between the contaminants and the iron surfaces. Only limited success has been achieved in the field, partly because the basic surface chemical reactions are not well understood. We are performing fundamental investigations of the interactions of the relevant chlorinated solvents, and trace element-containing compounds with single- and poly-crystalline Fe surfaces. The aim of this work is to develop the fundamental physical and chemical understanding that is necessary for the development of cleanup techniques and procedures.

Research Progress and Implications

As of May 1998, we have performed both bulk chemical measurements of the reduction reactions and surface science studies of model chemical systems. During these first two years of funding, we have made significant progress in both areas. Initially, we focused primarily on the reduction of selenate by elemental iron. We also performed some work with chromate, perchlorate, uranyl, and carbon tetrachloride. In the following sections some of our progress is described.

We studied the factors affecting the selenate reduction reaction to determine the optimum conditions for the remediation of wastewater. We characterized the effects of pH, O_2 concentrations, ionic strength and solution composition, degree of agitation, and iron surface pretreatment in solutions contaminated with 0.20 mg L^{-1} selenate (+VI oxidation state). The reaction was found to be first-order with respect to selenate concentration. Increases in either the pH or ionic strength decreased the rate of selenate reduction, with pH being the more important variable. The reaction was also sensitive to changes in the preparation of the iron and type of iron. Washing with 0.01N HCl and rinsing with O_2-free water resulted in the most reproducible surface for use in these measurements. Agitation of the iron/water suspension increased the rate of reaction. Palladium coated iron metal tripled the rate of selenate reduction. There was little or no reduction of perchlorate by either iron or Pd-coated iron. Carbon tetrachloride reduction was significantly faster in oxygenated water compared to O_2-free and was not inhibited by competitive adsorption of toluene or humic acid.

In order to probe the solid species formed by the reduction of selenate with iron filings, near edge x-ray adsorption fine structure (NEXAFS) analysis of reacted iron was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). Se was found on all of the surfaces in mixtures of the (0) and (+IV) oxidation states. Samples prepared under O_2 produced a greater amount of the (0) species, while samples prepared under N2 produced a greater portion of (+IV). Samples prepared at low pH had greater amounts of (0) than samples prepared at higher pH values.

X-ray diffraction (XRD) was used to determine the species of iron rust formed as a result of the reactions with zero-valent iron. The dominant product is lepidocrocite (g-FeOOH) with minor amounts of maghemite (g-Fe2O3). These are insoluble mineral forms of oxidized iron (+III oxidation state) that are suspended in the reaction solutions.

Bulk solution studies carried out with uranium and chromium have revealed that both can passivate the surface of iron. Depending on solution concentration, the reaction of uranium and chromium with iron can occur with no rust formation. This is important because of the implications of possible shutdown of the sorption and/or reduction reactions. Additionally, this passivation slows down the sorption and reduction of other trace elements. Chromium (as chromate) slowed down both the loss from solution and reduction of selenium (as selenate) by a factor of about 15. NEXAFS analysis indicated that uranium coprecipitated with selenium on the iron surface. However, the selenium was in the +VI oxidation state. This hasn't been observed in any other reactions with selenium and iron. Also, uranium seems to buffer the pH of the reaction solution, whereas other target oxyanions are associated with an increase in pH (> 9.0).

Previous studies have often overlooked the formation and reaction of green rust, which is a mixed +II/+III oxidation-state iron hydroxide mineral. It has a pyroaurite mineral structure with the anions substituting in the place of hydroxyl ions. Chloride, nitrate, sulfate, carbonate, and selenate have been reported to be in the structure of green rust. We've confirmed the presence of green rust formation in our reactions visually and chemically.

Studies of iron foils were carried out in order to utilize surface-sensitive techniques that can better characterize the surfaces. We used scanning tunneling microscopy (STM) to look at polycrystalline iron foils during the reduction of selenate, chromate and uranyl. This was done in-situ, using an STM that is designed for operating under solution. We found that, for all three reactions, the surface morphology changed from the roughened surface characteristic of iron oxides to a smooth surface. Note that a blank run using only water showed no changes. X-ray photoelectron spectroscopy (XPS) was used to measure Fe foils following the reduction of selenate, chromate and uranyl in aqueous solution. For all three species, films composed of partially reduced oxides were found. The reduction of U was found to be very sensitive to dissolved oxygen, while the reductions of Se and Cr are not. No changes to the native iron oxides were observed with XPS, due the inherent surface sensitivity of the technique.

In order to probe the reaction mechanism on an atomic scale, we have begun investigations of the reduction reactions of model gas-phase molecules with atomically clean iron in ultra-high vacuum (UHV). We began with the reaction of SeF6 with iron and iron oxide surfaces, as Se in SeF_6 is in the (+VI) oxidation state just as in selenate. Polycrystalline iron foils were cleaned in vacuum by sputtering with Ar^+ ions. The foils were then reacted with SeF_6 gas in a special UHV reaction chamber, and XPS was used to measure the iron foils following reaction. The spectra showed a large excess of fluorine, which indicates that the major reaction pathway involves the reduction of Se and its subsequent ejection from the surface. A small amount of adsorbed selenium does remain on the surface, which was found to be in a completely reduced form. An iron oxide was grown in-situ, and it was found to be largely unreactive to SeF6.

In summary, we have begun our program with a number of detailed investigations of the reduction of selenate, chromate and uranyl by reaction with Fe surfaces. Excellent collaboration between the Physics Department and the Department of Environmental Sciences has stimulated a wealth of new ideas for this and other environmentally-relevant projects.

Planned Activities

More bulk studies will be performed to determine the optimal operating conditions for reaction. This information will help determine which solutions will be later used for the surface science experiments. More NEXAFS will be done with other species, as the initial data collected following Se reduction was very useful. More STM and XPS will be performed using iron foils, but we will be first cleaning the foils with Ar^+ bombardment and then transferring the samples to the solution under an inert atmosphere. This will allow us to probe the actual reaction with zero-valent iron, rather than just measuring the native oxide overlayer. More detailed UHV work will also be performed in order to clarify the reaction mechanism. For example, we will repeat the SeF_6 experiments using Fe single crystals, which will eliminate grain boundary effects. We will also employ other volatile oxyanion reactants that can be reduced by iron, such as selenic acid and various chlorohydrocarbons.

Experimental Determination of Contaminant Metal Mobility as a Function of Temperature Time and Solution Chemistry

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Research Objective

The objective of this work is to determine the fundamental data needed to predict the behavior of ^{90}Sr at temperature and time scales appropriate to thermal remediation. Our approach combines macroscopic sorption/precipitation and desorption/dissolution kinetic experiments which track changes in solution composition with direct molecular characterization of Sr in the solid phase using x-ray absorption spectroscopy. These experiments will be used to identify mechanistic geochemical reactions and their thermochemical properties that will be incorporated into geochemical computer codes.

Research Progress and Implications

As of May 1998, we have completed most of our static sorption experiments as a function of temperature (25, 60, and 80ºC), solution pH (4 to 10), initial Sr concentrations (10-7 to 10-3 M), and partial pressure of CO_2 (100% N_2 or atmospheric CO_2). We chose to study goethite, kaolinite, gibbsite, and amorphous silica because iron and aluminum (oxy)hydroxides, aluminosilicate clays, and quartz are key components in soils, sediments, and aquifers. We have completed x-ray absorption analysis of Sr sorption to kaolinite and goethite at 25ºC, initial Sr of 10-3 M, and pH 9.

Strontium sorption to goethite, kaolinite, and amorphous silica is dependent on solution pH, with little or no sorption between pH 4 and 7, and increasing sorption from pH 8 to 10. No sorption occurred at the gibbsite-water interface from pH 4 to 10. Strontium removal from solution is catalyzed by reactions at the goethite, kaolinite, and amorphous silica surfaces, because minimal amounts of Sr where removed from solution without these solids in waters supersaturated with respect to strontianite ($SrCO_3$). Strontium sorption from 10-3 M Sr solutions at pH 10 and atmospheric CO_2 was greater to amorphous silica (100%), than goethite (50%) and kaolinite (20%). Strontium sorption to kaolinite and goethite is not dependent on temperature from 25 to 80ºC.

The dominant surface complexes, as determined by x-ray absorption spectroscopy (XAS), are outersphere hydrated-Sr complexes at the kaolinite-water interface and both outersphere hydrated-Sr complexes and reactive multinuclear Sr-carbonate complexes. For all of the kaolinite samples identical x-ray absorption spectra were obtained, yielding 6 to 9 first neighbor O atoms at an average distance of 2.60 Å. If innersphere or multinuclear complexes form we would expect to see second neighbor Al, Si, or Sr atoms in the x-ray absorption spectra. Outersphere hydrate-Sr complexes at the kaolinite-water interface appear to be very stable. Spectra from sorption experiments aged for two months showed only outersphere hydrated-Sr complexes. In solutions supersaturated with respect to strontianite, we had expected multinuclear Sr-carbonate surface complexes to form as the samples aged.

Strontium complex formation at the goethite-water interface consists of disordered multinuclear Sr-carbonate complexes in atmospheric CO_2 experiments and outersphere hydrated-Sr complexes in CO_2 free experiments. The multinuclear Sr-carbonate complex consists 6 to 9 first neighbor O atoms at 2.60Å, 1 second neighbor Fe atom at 2.04 Å, and 7 to 8 second neighbor Sr atoms at 4.1Å and 2 second neighbor Sr atoms at 4.88 Å. Interestingly, aging the goethite experiments with initial

atmospheric CO_2, yielded outersphere hydrated-Sr surface complexes identical to those observed in CO_2 free sorption experiments and the kaolinite sorption experiments. During aging, it is possible that dissolved carbonate diffused into channels in the goethite structure, lowering the degree of solution supersaturation with respect to strontianite, dissolving the Sr-carbonate surface complex and forming outersphere hydrated-Sr complexes.

Our results to date agree with field observations of ^{90}Sr mobility at Hanford, and show that Sr is a highly mobile element with minimal retardation at mineral-water interfaces. Furthermore, transport of Sr sorbed to Fe and Si colloids in pH 8 to 10 waters is likely. These colloids may form from iron and silica rich alkaline waste streams as the pH decreases due to dissolution reactions with the aquifer geology. Our results also suggest that a closely monitored amorphous silica reactive barrier buffered at pH 10 to 11 may effectively trap Sr at a contaminant plume front.

Planned Activities

For the remainder of this project (1.5 years) we will combine the solution chemistry and solid phase speciation to model strontium sorption as a function of temperature (25, 60, and 80ºC), solution pH (4 to 10), initial Sr concentrations (10-7 to 10-3 M), and partial pressure of CO_2 (100% N_2 or atmospheric CO_2). Our model will be based on the mechanistic geochemical reactions and thermochemical properties identified in our experiments, such that this information can be used to predict ^{90}Sr mobility at Hanford and potential radioactive waste repositories, and to optimize any clean-up programs.

Additional experiments include flow-through Sr sorption/desorption experiments to goethite and amorphous silica at pH 9 in solutions open to atmospheric CO_2. These experiments will be complimented with x-ray absorption spectroscopy experiments to determine solid phase speciation, including Sr speciation at the amorphous silica-water interface from the static sorption experiments.

Molecular-Level Process Governing the Interaction of Contaminants with Iron and Manganese Oxides

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Gordon E. Brown, Stanford University

Research Objective

We are carrying out a program of research that focuses on the fundamental mechanisms of redox chemistry of contaminants on mineral surfaces. As much of this chemistry in sediments involves the Fe(III)/Fe(II) and Mn(IV)/Mn(II) couples, we are focusing on mineral phases containing these species. We are using a variety of experimental probes, along with molecular modeling theory, to determine clean mineral surface structure and morphology, details of the chemisorption and decomposition of water, and the interface structure and redox chemistry of important contaminants such as CrO_4^{-2} on these surfaces. Insight gained in this project will aid in the formulation of more accurate and realistic contaminant-surface complexation and contaminant transport models, and may suggest improved remediation strategies for certain kinds of contaminated soil and groundwater.

Research Progress and Implications

In what follows, we highlight the most important results obtained from June 1, 1997 to June 1, 1998, the second year of this three-year project. Detailed comparison of scanned-angle photoelectron diffraction (PED) measurements taken at the Advanced Light Source (ALS) with simulations employing quantum mechanical scattering theory reveal that a-Fe_2O_3(0001) (hematite) is terminated with a single layer of Fe atoms, and that the percentage relaxations of the first four layers are -41%, +18%, -8% and +47% of the respective bulk values. These rather large surface relaxations, which are similar in both magnitude and sign to those determined to exist on a-Al_2O_3(0001), are driven by the associated decrease in surface energy. We have calculated the surface energies of relaxed and bulk-terminated (unrelaxed) a- Fe_2O_3(0001) to be 1.64 and 4.24 J m^{-2}, respectively. An implication of this finding is that it is an outer layer of Fe(III) on basal-plane hematite that interacts with water, toxic anions and organics, rather than oxygen, as expected based on conventional wisdom. Scanning tunneling microscopy (STM) reveals that the Fe_3O_4(001) (magnetite) surface is terminated exclusively by either a tetrahedral iron or an octahedral iron layer with lattice oxygen, but not by both. Given that both the coordination number and the charge states of the iron in these layers are different, significant differences in the surface chemistry are expected depending upon the terminating layer. Determining which atomic layer constitutes the surface is the focus of both PED and STM experiments in the immediate future. Dramatic differences in the surface step density of Fe_3O_4 (001) can be achieved by using different MBE growth conditions. The resulting step densities (defined as the ratio of the number of atoms at a step edge to the total number in the surface) can vary from as high ~0.20 to lower than 0.05. The ability to systematically vary the step density is crucial to ultimately understanding the role of steps in the redox chemistry that occurs between magnetite and toxic anions and chlorinated organics. The measured threshold water vapor pressure s for the hydroxylation of a-Al_2O_3(0001) and a-Fe_2O_3(0001) surfaces have been measured by soft x-ray photoemission at the Stanford Synchrotron Radiation Laboratory (SSRL) to be 1 torr and 10E-4 torr, respectively. While the measured threshold pressure for a-Al_2O_3 is similar to the calculated threshold pressure for the conversion of a-Al_2O_3 to $Al(OH)_3$ based on an equilibrium thermodynamic model, the measured threshold pressure for a-Fe_2O_3 is more than five orders of magnitude lower than the calculated threshold pressure for the conversion of a-Fe_2O_3 to FeOOH or Fe(OH)3. This result is most likely due to the higher acidity of surface Fe(III) on a-Fe_2O_3(0001) relative to that of surface Al(III) on a-Al_2O_3(0001), which is corroborated by our molecular mechanics calculations. The reaction of water with (001) and (111) surfaces of natural Fe_3O_4 prepared in ultrahigh vacuum was monitored using chemical shifts of O 1s and Fe 2p core-level photoemission spectra. We found that the initial reactions of water with these surfaces are quite similar to those for the a-Fe_2O_3(0001) and (1-102) surfaces and involve dissociation of water, indicating almost identical and small sticking coefficients. However, while hydroxyl coverages for a-Fe_2O_3 remain in the submonolayer range for water doses as high as 10E9 Langmuir, the Fe_3O_4(001) and (111) surfaces react very strongly with water, resulting in hydroxylation extending several layers deep. Cr L2,3-edge and O K-edge x-ray absorption fine structure (XAFS) studies, also carried out at SSRL, of the reaction of aqueous CrO_4^{-2} with Fe_3O_4(111) reveal that Cr(VI) in chemisorbed CrO_4^{-2} is very quickly reduced to Cr(III), and that the surface converts into a goethite-like phase. Grazing-incidence x-ray absorption fine structure (GI-XAFS) studies of CrO_4^{-2} on partially reduced a-Fe_2O_3(0001) reveal that substantial reduction of Cr(VI) to Cr(III) occurs. An implication of this result is that both magnetite and partially reduced hematite are effective at converting toxic, bioavailable Cr(VI) into less toxic and less bioavailable Cr(III). We have developed pulsed-laser photoacoustic spectrosc copy at the Environmental Molecular Sciences Laboratory (EMSL) to nondestructively monitor the levels of Cr(VI) in solutions contacting iron oxides. Initial experiments reveal that the technique can be used to: (i) measure adsorption affinity of anions on hematite surfaces, (ii) monitor the rate of Cr(VI) adsorption on hematite powder in real time, and, (iii) study the effect of competing anions, specifically phosphate, sulfate, and carbonate, on Cr(VI) uptake. Significantly, we now have a new tool to determine the effect of nontoxic, naturally occurring anions in blocking sorption sites for Cr(VI) on iron oxide surfaces.

We have developed a molecular mechanics model to predict the protonation/deprotonation energetics of the adsorption of oxoacids on solvated Fe oxide surfaces with realistic proton

stoichiometries. This model was tested against hydrated Fe(II)- Fe(III)-(Cr,P,Si)O_4-H_2O crystal structures with generally good results, yielding lattice constants within 5% of experiment. The ability of this model to account for both the structure and protonation energetics in the tetrahedral oxyanions is remarkable and makes the ionic model a feasible option for future investigation of surface complexation reactions using molecular dynamics techniques. We have conducted exploratory work on the synthesis of thin-film pyrolusite (beta-MnO_2) on TiO_2(110) at the EMSL. Well-ordered, pseudomorphic overlayers form for substrate temperatures between 400°C and 500°C for coverages of up to 6 bilayers. Thicker films rapidly disorder due to the simultaneous formation of pyrolusite and ramsdellite, which is orthorhombic and not lattice matched to TiO_2(110). However, thin films of rutile pyrolusite are preferentially stabilized by the TiO_2 substrate. Being able to prepare these well-defined surfaces allows us to begin experiments to determine their redox potential compared to that of the Fe oxides.

Planned Activities

Immediate future activities will focus on high-resolution STM imaging at EMSL, PED at the ALS, and crystal truncation rod (CRT) x-ray scattering studies at the Advanced Photon Source (APS) of clean and water-exposed hematite and magnetite surfaces to determine the structural modifications caused by the hydroxylation process. We plan to fully analyze our GI-XAFS data on the interaction of Cr(VI) on synthetic thin-film hematite samples (reduced and unreduced) collected in March 1998, and to extend these studies to Cr(VI) interactions with thin-film magnetite. This work should lead to a model of Cr(III) surface complexes on reduced hematite and magnetite. We also plan to initiate a study of the reaction of TCE in solution with magnetite surfaces using C K-edge and Cl L-edge measurements. Our future LPAS experiments will focus sorption kinetics and equilibria measurements for Cr(VI) sorption on the MBE-synthesized hematite and magnetite thin films at ultra-trace levels of Cr(VI). Using our Fe(II,III)-(Cr,Si,P)O_4 potentials, which have now been rather rigorously tested on crystalline solids, in conjunction with our iron oxide-water potential models, we will conduct molecular dynamics investigations of chromate sorption to solvated hematite and magnetite surfaces. We plan to grow a-Fe_2O_3(0001) with substitutional Al by MBE, in order to determine the effect of this geochemically important impurity on redox chemistry.

Other Access To Information

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13. S. Thevuthasan, W. Jiang, D.E. McCready, and S.A. Chambers, "Rutherford Backscattering and Channeling Studies of Mg and Fe Diffusion at the interface of g-Fe_2O_3(001)/MgO(001) ", in preparation, (1998).
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5. (invited) S.A. Chambers, "Surface and Interface Structure of MBE-Grown Fe and Mn Oxides", Naval Research Laboratories, Washington D.C., May 1998 .
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Sorption of Heavy Metals and Radionuclides on Mineral Surfaces in the Presence of Organic Co-Contaminants

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George Redden, Stanford University

Research Objective

This project is designed to determine how organic chelating ligands can influence the partitioning of ionic solutes (heavy metals and radioactive isotopes) between the solution phase and metal-oxide surfaces. Equilibrium states and kinetics of partitioning in these ternary systems will control contaminant transport and bioavailability of the ligands and contaminant metals in groundwater. As a result, this work represents a significant contribution toward efforts to develop predictive modeling for the transport and transformation of groundwater contaminants.

Uranium(VI), strontium(II) and lead(II) have been chosen as representative of high priority pollutants at DOE and non-DOE sites. Strontium in particular has received relatively little detailed attention in the literature. Mineral surfaces chosen for this project include goethite, gibbsite, and kaolinite. The organic chelators - EDTA, NTA, and citric acid - are components of both DOE and industrial wastes. In addition, citric acid is found naturally as a product of metabolic processes in soils and groundwater.

Research Progress and Implications

Project Status as of June 1, 1998:

Uranyl | Citrate | Solid phase systems - Macroscopic equilibrium studies

Results for the batch studies involving uranyl, citrate, and the three mineral phases (goethite, kaolinite, gibbsite) have been summarized and published by Redden, et al. (1997). This part of the project demonstrated that the effect of citrate on uranyl sorption can be dependent on the nature of the solid phase and can be highly variable. A particularly interesting observation concerned the goethite system where citrate dramatically increased uranyl sorption in the low pH range and that the extent of the effect appeared to be dependent on the citrate:surface ratio. The implication is that uranyl is unaffected by citrate until a critical surface concentration is achieved at which point it is possible that the positive surface charge has been significantly reduced (and can be negative even at pH 3.5) and carboxylic acid groups are potentially more available for complexing with uranyl.

Uranyl | Citrate | Goethite system - Phenomenological studies

Biodegradation: It was noted previously that biodegradation of citrate in these experiments can be a problem - or perhaps a useful feature. For longer term experiments where dissolution of the solid phases will be studied, it is necessary to prevent degradation of citric acid. We have been able to reduce or eliminate this risk by taking precautions to maintain sterile conditions (combination of autoclaving and filter sterilization).

Biodegradation of the organic ligand in the presence of heavy metals and solid phases, and the ultimate fate of the metal is an intriguing question in itself. Although this is beyond the primary scope of this study, we have conducted very brief scoping studies to look at the degradation of citric acid in the presence of a sorbing solid phase, and to see if an organism can be isolated that acts on uranyl (redox) in a medium containing citric acid.

Proton Stoichiometry: The proton stoichiometry of citrate sorption on goethite has been described previously. This information will be used to develop a consistent picture of the nature of citrate sorption along with the spectroscopic studies. We are particularly interested in issues of surface charge and available surface-bound carboxylic acid groups.

Ionic strength: Variations in surface partitioning as a function of ionic strength is generally considered to be indicative of the type of surface complex. Strong covalent surface complexes are assumed to be unaffected by changes in ionic strength while weaker outer-sphere complexes are displaced by increasing ionic strength. We have made the unusual observation that increasing ionic strength actually increases uranyl partitioning in the presence of citric acid. The hypothesis is that screening of the net positive surface charge reduces the free energy of the interaction between the uranyl cation and the negative surface-bound citrate groups.

Electrophoretic mobility: We have measured changes in electrophoretic mobility of goethite particles as a function of citrate concentration at pH 3.5, and as a function of pH at a relatively high citrate concentration. The relative changes in mobility have demonstrated that citrate effectively reduces goethite surface charge and can produce a negatively charged surface even at pH 3.5.

Sorption/Desorption: The complexity of the interaction between citric acid and the goethite surface is unknown. It is reasonable to expect that once sorbed, the nature of the complexation can change with time, and that ligand promoted dissolution of the surface can occur. We are conducting studies to determine whether the rate and extent of citric acid desorption varies as a function of pre-equilibration time. We expect the desorption process will become progressively slower as pre-equilibration time increases. The first results have shown this to be the case. We will be particularly interested in whether a complete mass balance for citrate can be verified.

Uranyl | Citrate | Goethite system - Spectroscopic Studies

FTIR: The first part of an FTIR study of citrate surface complexation was conducted at the beginning of this project with colleagues at the Umeå University in Sweden. In that study, it was possible to demonstrate that a covalent surface complex was formed and that uranyl was at least partially associated with surface-bound citrate, however this first study was constrained by sensitivity limitations. A second and concluding study is planned for this summer. An advanced ATR cell (attenuated total reflectance), and anticipated improvements in instrument performance should make it possible to obtain more complete spectroscopic information about the nature of the citrate-surface bonding, the state of uncomplexed carboxylic groups, and whether uranyl is associated with the citric acid.

EXAFS: An EXAFS study (Extended X-ray Absorption Fine Structure spectroscopy) of the uranyl-citrate-goethite system was started in May of this year at the DOE supported Stanford Synchrotron Radiation Laboratory. This study is intended to compliment the FTIR study by providing information about that local environment of uranyl in the presence of citric acid. Results from the first of three planned experimental sessions were considered very good from the standpoint of data quality and sensitivity. Preliminary evaluation of the spectra shows distinct qualitative differences between model systems (e.g., uranyl, uranyl-citrate, and uranyl-goethite systems) and the uranyl-citrate-goethite system in several pH regimes. Although our original working hypothesis has been that citrate is involved in a goethite-citrate-uranyl ternary complex, the EXAFS results suggest that, at least under the conditions under which the samples were prepared, the system may be better represented by multiple uranyl surface complexes and that uranyl may act as a bridge between goethite and citrate.

These results along with the demonstration of good sensitivity for lower uranyl concentrations are now being used to design systems for the second set of EXAFS analyses.

Lead | EDTA, citrate | Goethite system - Macroscopic equilibrium studies

Based on the relatively extensive scrutiny of the goethite-citrate-uranyl system, the analogous system with lead EDTA, and citrate are now being studied. Batch sorption experiments are being run

to determine whether a corresponding behavior for lead can be observed, and to extend the system with a chelating ligand that is significantly different from citrate. Based on past work we expect that biodegradation of EDTA will be less of a problem although the same precautions will be exercised to ensure sterility of the systems.

Lead | Carbonate | Goethite system - Macroscopic and Spectroscopic studies

Most relevant natural systems will have carbonate as a significant solution component due to mineral, atmospheric and biological sources. It is very likely, given the chemical similarities between carbonate and organic carboxylic groups, that carbonate solution species will influence the degree to which organic ligands affect metal partitioning. An extensive study of carbonate sorption on goethite is nearing completion. This is now being extended to a study of the effect of carbonate on lead sorption using batch sorption experiments and ATR-FTIR analysis of the surface bound complexes.

Strontium | Ligand | Solid phase systems - Preliminary modeling studies

System involving strontium have received little attention to date. Sorption of strontium in the presence of citrate and EDTA, and in systems with goethite, gibbsite, and kaolinite, are being initiated using the methodologies developed for the goethite-citrate-uranyl system.

Planned Activities

Planned Activities and approximate timetable:

Macroscopic sorption studies (following protocols developed for the uranyl-citrate-goethite system):

Citrate desorption kinetics => present through August, 1998.
Lead-citrate-goethite system => present through March, 1999.
Lead-EDTA-goethite system => present through June, 1999.
Lead-ligand-gibbsite,kaolinite systems => November, 1998 through June, 1999.
Strontium-ligand-solid systems => July, 1998 through June, 1999.
Lead-carbonate-goethite system => present through November, 1998.

Spectroscopic studies:

EXAFS study of the Uranyl-citrate-goethite system => July, October 1998
FTIR study of the Uranyl-citrate-goethite system => November, 1998
FTIR study of the lead-carbonate-goethite system => present through September, 1998.

Additional selective FTIR and EXAFS studies are anticipated depending on results from macroscopic experiments.

Characterization of Contaminant Transport Using Naturally-Occurring U-Series Disequilibria

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Research Objective

The goal of the research is to study the migratory behavior of contaminants in subsurface fractured systems using naturally occurring uranium- and thorium-series radionuclides as tracers under in-situ physico-chemical and hydrogeologic conditions. Naturally occurring U- and Th-series disequilibria can provide information on the rates of adsorption-desorption and transport of contaminants as well as on fluid transport and rock dissolution in a natural setting. We are developing a realistic model of contaminant migration in the Snake River Plain Aquifer beneath the INEEL by evaluating the retardation processes involved in the rock/water interaction. The major tasks are to: 1) determine the natural distribution of U, Th, Pa and Ra isotopes in the groundwater as well as in rock minerals and sorbed phases, and 2) study rock/water interaction processes using U/Th series disequilibria and a statistical analysis-based model code for the calculation of in-situ retardation factors of radionuclides and rock/water interaction time scales. This study will also provide an improved understanding of the hydrogeologic features of the site and their impact on the migration of contaminants.

Research Progress and Implications

This report summarizes results after 20 months of a 36-month project. Studies performed at LANL include analysis of the long-lived nuclides ^{238}U, ^{235}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{232}Th, and ^{231}Pa by thermal ionization mass spectrometry (TIMS). Studies performed at the University of Southern California include the measurement of short-lived naturally occurring radionuclides by decay-counting techniques and the development of models to predict the migration behavior of these radionuclides. Initial efforts began with analysis of 31, 0.5L water samples obtained through routine sampling by USGS and INEEL personnel. One significant observation from these data is that $^{234}U/^{238}U$ activity ratios are highest in waters that emanate from local recharge areas to the northwest of the INEEL and they decrease in the direction of groundwater flow. Contours of high $^{234}U/^{238}U$ ratios delineate preferential flow paths extending southward from the local recharge areas. Our uranium data have allowed delineation of these preferential flow pathways in greater detail than obtained by other methods. The contour map of $^{234}U/^{238}U$ ratios also identifies isolated pockets with low $^{234}U/^{238}U$ ratios. These are suspected to represent groundwater which has undergone more extensive water/rock interaction as a result of either longer residence times of faster reaction rates. These results are important for understanding the hydrologic context of the site and crucial for interpreting our complete data sets for the U and Th decay chains.

Because we found insufficient Th, Pa and Ra in the small samples obtained through routine USGS sampling, we had to modify our sampling strategy in order to obtain samples sufficiently large to allow measurement of the short- and long-lived nuclides of the U and Th decay chains. This effort was not anticipated in our original research plan, but we have successfully collected large-volume groundwater samples (~1000 liters) from 12 wells from the site. Radioisotopes of thorium (^{232}Th, ^{230}Th, ^{228}Th, and ^{234}Th), radium (^{226}Ra, ^{228}Ra, and ^{224}Ra) and polonium (^{210}Po) were pre-concentrated in the field by passing the samples through two cartridge filtration units (connected in series at each well) containing MnO_2-impregnated acrylic fiber adsorbers. An additional 12L of water was collected for Th, Pa and Ra concentration measurements by TIMS. We have now obtained a full suite of U- and Th-series nuclides from these large-volume samples. Isotope ratio plots show some clear trends.

In general, the degree of disequilibria among the U, Th and Ra isotopes decreases along flow pathways and away from local recharge drainages to the northwest of the site. The short half-lives of some of these nuclides (e.g., ^{224}Ra $t_{1/2}$ = 3.66 days) indicates that adsorption/desorption must be important in controlling some of the isotope ratios. Trends among more conservative, long-lived species (e.g., U) are taken to reflect mixing and allow estimation of relative volumes of different groundwaters.

We have successfully estimated the degree of retardation due to rock-water interaction in the groundwater system at INEEL by modeling the observed radioactive disequilibria. Our model results indicate that adsorption of radium by the aquifer solids at the site takes place on time scales of a few tenths to several seconds, about 1-2 orders less than those of thorium. The desorption times, on the other hand, are several days for radium and several years for thorium. Based on these sorption-desorption rate characteristics, we estimate that retardation factors (i.e., the ratio of flow rate of fluid to those of dissolved radionuclides) are of the orders of 106 for ^{230}Th, 104 for ^{226}Ra, and 103 for ^{238}U. The model predicts that radionuclides sorbed on solids, which are exchangeable with the dissolved species through sorption/desorption, play an important role in affecting the decay-series disequilibrium in groundwater systems. The model also indicates that the major source of ^{222}Rn in groundwater from the study area originates from decay of ^{226}Ra sorbed on aquifer solid surface, rather than the previously held notion of direct alpha recoil from the solid ^{226}Ra pool.

The retardation-factor estimates that we have derived contribute to our understanding of the disposal and migratory behavior of radioactive wastes at INEEL. These estimates allow us to delineate a rather large range of migration rates for possible contaminants in groundwater at the site and suggest that three groups of wastes can be identified in terms of their mobility. The migration of radionuclides with high ionic potential (readily hydrolyzed) such as thorium and lanthanide fission products is heavily retarded. The degree of retardation for alkali- and earth alkali-radionuclides (e.g., ^{133}Ba, ^{90}Sr,and ^{137}Cs), is such that these nuclides are unlikely to be transported far away from the contaminated areas. Uranium (and perhaps many transuranic radionuclides) displays relatively high mobility in the aquifers we have studied.

Planned Activities

In the coming months we plan to analyze ^{210}Pb in the samples at hand. Plans are being formulated to carry out additional large-volume groundwater sampling from other wells at the site, and to collect samples of ~5-liter size for the measurement of ^{222}Rn in order to further constrain the alpha-recoil input of radionuclides to the groundwater medium. Upon completion of the fluid analyses, we also intend to obtain information on the activities of U, Th, Ra and Pb in rock samples from drill cores retrieved by the USGS - information that is germane to our modeling the transport in the study area. Fourteen samples from two cores have been collected and we plan to sample a third. The model code for contaminant transport will be further developed using these new data.

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Hydrologic and Geochemical Controls on the Transport of Radionuclides in Natural Undisturbed Arid Environments as Determined by Accelerator Mass Spectrometry Measurements

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Research Objective

This research develops techniques for measuring globally distributed radionuclides occurring today in extremely low abundances ("fallout" from the era of atmospheric nuclear testing), and then applies these techniques to better understand the mechanisms by which radionuclides migrate. The techniques employ accelerator mass spectrometry (AMS), a relatively new analytical tool that permits this work to be conducted for the first time. Because the nuclides addressed in this project originated from thermonuclear events, they are generally those of most concern when assessing the extent of and risk from actual or potential radioactive contamination. The advantages of our approach include: 1) the ability to conduct migration studies in locations most like those of concern to public health, e.g., a "far-field" environment; 2) sites of multiple contamination, e.g., by VOCs, can be avoided; 3) it becomes unnecessary to collect research samples that are themselves radioactive waste and are therefore difficult to handle and dispose of in the laboratory; and 4) since the nuclides are globally distributed, migration research can be conducted in any chosen environment.

Research Progress and Implications

This report summarizes the research progress through the first 16 months of a 3-year project. It discusses the work completed and in progress on the development of AMS techniques for ^{99}Tc, ^{129}I, ^{36}Cl, and the development of a demonstration field site chosen for this project in arid unsaturated soils.

Development of AMS ^{99}Tc Techniques. Prior to our EMSP work, no group to our knowledge had rigorously attempted to develop AMS for ^{99}Tc measurements. This lack of precedence, and some specific technical difficulties related to the lack of a stable Tc isotope, presented a number of challenges and questions. We have shown that acceptable Tc- negative ion currents can be produced in the AMS cesium sputter source (ionization efficiency of about 1E-03). We have also demonstrated an ability to reject 99Ru, a stable isobaric interference, using our characteristic projectile x-ray detection system. An unanticipated problem was discovered in this process: S ions can combine with Cu or Zn ions to create isobaric interferences in the AMS system. We have addressed this in two ways. First, we added a thin gas ionization detector immediately before the x-ray detection system. Only masses with the appropriate energy loss (δ-E) and x-ray emission for Tc are measured. Second, we now use TcO-, rather then Tc-, as the ion injected into the accelerator, which reduces the background by approximately two orders of magnitude. This significantly improves the sensitivity of our detection limit. In full analytical mode, we anticipate detection limits in the range of 10-100 femtograms of Tc.

Currently, our efforts center around the choice of an appropriate analytical matrix and dilution reference isotope, and the conversion of Tc in solution to a solid form for introduction into the ion source. We have tried and rejected both Rh and Ag as analytical matrices, although we have determined that either may be suitable with the planned implementation of new system control options. We are now using Nb for a matrix which shows good promise in initial tests. Preliminary results with Tc spikes showed ±20% reproducibility over two orders of magnitude, and for 5 widely varying sample preparation procedures. The standard deviation for blanks was equivalent to ±10 fg, and was dominated by trace Ru in the Nb stock. The background was 40±9 fg for a 1mg Nb sample. Correction of the results to account for the Ru is expected to further lower both the standard deviation of the blanks and the background. We have removed and detected ^{99}Tc from spiked soils from the field area by these methods, and are now in the phase of this project of debugging and streamlining certain steps in our analytical method.

Development of AMS ^{129}I Techniques. We have made significant improvements in iodine sputtering efficiency, beam current maximization, detection efficiency, and elimination of isobaric interferences. We now believe reliable ^{129}I analyses can be made at a background level of ^{129}I/I = 1E-13. This is more than adequate to measure natural ambient ^{129}I/I levels in arid soils, and certainly adequate to measure anthropogenic levels. To demonstrate this, we performed two experiments. First, we measured ^{129}I concentrations in soil sample IAEA-375 originating from Chernobyl, and having a ^{129}I concentration of 1.2E09 atoms/gram (as determined by neutron activation to 20% accuracy). Within analytical uncertainties there is good agreement between our AMS measurements and those determined by the IAEA. Unfortunately, no "standards" exist that contain ^{129}I concentrations in the low AMS range (i.e., below neutron activation capabilities). Therefore for a second experiment we made repeated measurements of a soil sample that serves as a proxy to those at our field site. It contains fallout ^{129}I in concentrations measurable only by AMS. Because no "accepted" value for ^{129}I concentration exists for this soil, we cannot judge the accuracy of our measurements. However, we can judge the precision of the measurements, and this is very good. Four of the 6 measurements agree within analytical error, and a fifth agrees within 20 percent. A sixth measurement was considerably lower than the others, but we believe this could be attributed to soil heterogeneity.

We are particularly concerned with the physical location of the iodine within soil samples. Speciation and complexing can result in either retardation or enhancement of migration. We have therefore conducted a series of sequential leaching experiments employing ammonium acetate (pH=8.2; pH=4.7), hydroxylamine hydrochloride, acetic acid, and ammonium carbonate. The soils undergo a sequence of 5 leaching steps. Initial results indicate that <20% of the ^{129}I is leachable in water alone. This low result is somewhat surprising since iodine is regarded as a "conservative" species that readily migrates with water. Further, even smaller amounts are leachable in either mild base or acid solutions (strong solutions completely strip the ^{129}I). Although these are only initial results, it may be the case that considerable ^{129}I in the soil is fixed on clays or in organic matter.

Development of the Field Site: Unsaturated Zone Trench. Rather than taking samples from drillhole cores, we chose to excavate a 5m deep trench (20m length, 18m width) and sample from the trench wall. This provides the ability to sample adjacent to soil structures that might affect soil moisture flux and radionuclide transport. The trench is located on the Nevada Test Site, adjacent to the Carpetbag geological fault. This site was chosen because previous work had shown the existence of significant structural features in these soils, probably due to fault activity. Samples were collected in six vertical profiles from land surface to the bottom of the trench. Samples were taken every 25cm, which allowed both thorough spatial coverage and a complete sampling of all levels of soil stratigraphy. All soil units were sampled by this strategy. Two of the profiles were "baseline" profiles that intersected no structural features of the soil. The other four profiles sampled obvious fractures in the soil: one containing abundant carbonate infill, one containing moderate carbonate, one free of carbonate, and the final profile - along the "contact" of the carpetbag fault - was a carbonate/soil interface. The two fractures not filled with carbonate contained abundant plant roots.

Moisture Flux at the Field Site: Cl and ^{36}Cl Distribution. The trench method of sampling provides very good geologic/hydrologic control for the distribution of the parameters that determine moisture and radionuclide flux. Concentrations of Cl at the field site are uniformly low, about 5-10 times lower than most similar arid sites. Maximum Cl values occur at depths between 2 and 3.5m, which is

1-3m shallower than similar sites in the region. The depths are not obviously correlated with soil structures. The lower concentrations result in calculated Cl ages that are 5-10 times younger at a comparable depth than similar sites regionally. Soil moistures are similar to those regionally, except for the zone <3 meters which is ~1.5 times the other sites. The moisture profiles combined with low Cl concentrations results in calculated moisture flux values significantly higher than regional expectations. The peak in fallout ^{36}Cl occurs between 1.5-2.2m, with profiles along fractures consistently deeper. These are similar depths to those reported in other studies. Neither Cl nor fallout ^{36}Cl appears to be correlated with soil particle size; although further particle characterization is continuing. As with almost all such published profiles, the Cl age at the depth of the fallout ^{36}Cl peak is significantly higher than the 40-50 year age of the ^{36}Cl peak. In order to reconcile the age disparity, the regional flux of Cl to the Earth's surface must be increased by a factor of five. Given current best estimates of atmospheric ^{36}Cl production, this seems unreasonable. The only other alternative appears to be a decoupling of Cl migration, with some Cl (here represented by the fallout Cl) migrating at a different rate than other Cl (here, the non-fallout Cl). While apparently enhanced by soil structure, the cause of the decoupling seems unrelated to all soil parameters measured or observed thus far. The existence of such decoupling would have significant implications for estimates of both moisture and radionuclide flux in arid soils. This will be the focus of further field work, numerical modeling of the flux, and the other radionuclide measurements to be made in this project.

Planned Activities

We now have the framework and confidence in our analytical techniques to begin ^{99}Tc and ^{129}I measurements on soils from the field site, with completion expected within a few months. We then will begin development of techniques for AMS measurement of ^{90}Sr and ^{93}Zr (or actinides). We are also now in a position to begin constructing a numerical model, using the NUFT unsaturated transport code, simulating the observed movement of moisture and fallout radionuclides at the field site. Full completion of this model is not expected until mid- to late-1999.

Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes

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Research Objective

The goals of this study are: (1) to elucidate the basic mechanisms by which potassium permanganate oxidizes common chlorinated solvents, various constituents in aqueous solution, and porous-medium solids, and (2) to assess the potential for chemical oxidation by potassium permanganate to serve as a remedial scheme involving either source zone flooding or reactive barriers. The combined theoretical and experimental study is designed to contribute fundamental knowledge about reaction pathways, reaction rates, specific intermediates formed, and controls on reaction processes. The specific objectives of this study are: (1) to describe through batch experiments the kinetics and mechanisms by which potassium permanganate oxidizes dissolved tetrachloroethene (PCE), trichloroethene (TCE), and dichloroethene (DCE), (2) to examine using column studies the nature and kinetics of reactions

between potassium permanganate, residual DNAPLs (PCE, TCE, and DCE) and porous medium solids, (3) to represent the process understanding in flow and transport models that demonstrate the potential applicability of the approach, and (4) to apply the resulting computer code in the development of appropriate field tests for assessing the approach.

Research Progress and Implications

Approaching the end of Year 2 of this 3-Year project, we can report significant progress in meeting the objectives of the study. Through a series of batch experiments, it has been shown that permanganate oxidation is effective in degrading various chlorinated ethylenes in aqueous solution. The disappearance of chlorinated ethylenes can be simply characterized by a pseudo-first-order model. Degradation half-lives for TCE, cis-1,2-DCE, trans-1,2-DCE and 1,1-DCE reacting with 1mM MnO_4^- range from about 24 s to 18 min. Degradation of PCE is much slower with a half-life of about 257 min. Overall, the degradation rate is inversely proportional to the number of chlorines present as substituents on ethylenes. These rates of degradation are impressive given the fact that the experiments were run with MnO_4^- concentrations only a factor of 10 or so greater than that of the particular chlorinated ethylene. It would be feasible in practice to increase rates of reaction by increasing MnO_4^- concentrations.

Our experiments also showed how the efficiency of degradation is reduced due to competition from other organic compounds. Contaminated ground water was synthesized as a mixture of ground water and landfill leachate. Three experiments were run with a fixed TCE concentration of 2 mg/L, a concentration of other organic compounds of 101 mg/L (TOC) and concentrations of MnO_4^- of 20, 80 and 120 mg/L. As expected, the competition for MnO_4^- led to a reduction in the reaction rate, as compared to experiments with TCE in Milli-Q water. However, with the largest MnO_4^- concentration, the competition appeared to be offset by other processes that effectively increased the degradation rate of TCE. Our preliminary assessment is that colloidal MnO_2 was catalyzing reactions between MnO4- and TCE. We will explore this aspect of the study in the coming year.

Early in the study, we confirmed previous work that indicated TCE degraded completely to CO_2 in a series of three steps. However, little was known about the overall reaction pathways and intermediates that formed. Preliminary indications were that TCE reacted with MnO_4^- to produce a cyclic complex, then carboxylic acids, and finally CO_2, along with Cl- and MnO_2. Of particular interest in our work were steps two and three. We undertook kinetic experiments with radiolabeled TCE (i.e., 1,2-^{14}C) to understand these reactions.

In the initial step, an organometallic compound (cyclic hypomanganate ester) is formed via the insertion of a p bond in the carbon-carbon in the carbon-carbon double bond into the metal-oxo bond of permanganate. This initial reaction is a rate-limiting step in the overall set of reactions and is not pH dependent. In the second step, the decomposition of the cyclic ester (Mn-V) proceeds via different reaction pathways to form various carboxylic acids. The particular acids that form depend upon the experimental conditions. At low pHs, formic acid is the dominant compound. At high pHs, glyoxylic and oxalic acids dominate. Kinetically, step 2 is a very rapid process with decomposition rates approximately 100 times higher than the formation rate.

All carboxylic acids formed in the second reaction step will be eventually oxidized to the final product, CO_2. Thus, the third step completes the overall degradation reaction. In the pH range 4-8, permanganate ion mainly reacts with the anionic species of the carboxylic acids, which is good agreement with our kinetic model. Thus, pH conditions affect the accumulation rate of CO_2. We developed an overall kinetic model that describes the loss and gain of compounds through the sequence of reactions.

The results of these experiments have important implications as far as the development of permanganate oxidation schemes as a remedial technology. Rapid and complete dechlorination is possible in reacting various chlorinated ethylenes with MnO_4^-. The reaction scheme does not yield the same intermediates, as is the case with reductive dechlorination. The main intermediates are four carboxylic acids including: formic, oxalic, glyoxylic and glycolic acids. Under conditions where permanganate is not present in excess and some of these acids end up in solution, they should be relatively mobile.

In general, the laboratory studies continue to support the continued development of permanganate oxidation schemes for the treatment of solvent spills. Issues, however, remain to be addressed. Foremost among them is the extent to which plugging by MnO2 may interfere with flushing schemes. Our work to date on dissolved compounds has an obvious extension to problems of pure phase liquids, which is how the solvents occur at many sites. The most important problems to consider in this respect are the rate limiting steps in the dissolution of free products and the effect of phase saturation on relative permeability and displacement efficiencies.

The fate and transport modeling for this study are being undertaken in Albuquerque, NM by Dr. Zhang of Duke Engineering Services. Dr. Zhang has developed a 3-D flow and transport code. The three-dimensional model simulates ground water flow and reactive transport of dissolved TCE, permanganate (MnO_4^-), end products (CO_2, MnO_2 and Cl^-), and various intermediate products (COOH, $[COOH]_2$, and others) away from a residually saturated TCE NAPL source. The flow and transport equations were formulated and solved using a control-volume finite-element method. Accordingly, mass balance can be calculated for each node and each species in the simulation domain. By formulating the kinetic-reaction processes as a single equation, it easier to couple the kinetic reactions and mass transport equations. The dissolution of NAPL was also treated kinetically using a mass transfer coefficient model. The reactive-transport equations for each species were coupled using a sequential iteration procedure in which the reaction rate term is calculated using concentrations at the previous time step and at the previous iteration of the current time step. Two different schemes, Strang operator splitting and Newton-Raphson, are being examined to compare their iteration efficiencies and memory requirements. Illustrative simulation trials have been conducted with the code to support on oral presentation at AGU. The rate constants used in the simulations were determined through our batch experiments. Preliminary simulation results show that significant quantities of TCE can be oxidized in a relative short period of time within short transport distance in the two cases. The model correctly predicts the formation of intermediate products at early times, as the oxidization process proceeds.

We are now in the process of comparing our simulation results with column experiments in which permanganate flooding is being used to remove TCE. Additional experimental data will become available from our own laboratory studies, later this year. Overall, there are two papers in press and one nearly ready for submittal, which is concerned with the reaction pathways. In the next few months, the first work related to the model studies should be submitted.

Planned Activities

In the coming year, we will undertake detailed column studies to better understand DNAPL dissolution processes. These experiments will be undertaken with thin rectangular columns to facilitate optical monitoring as well as conventional monitoring. Of particular interest is the relative efficiency of flushing and the factors that control the flushing and the extent to which solid products may lead to plugging. We will examine multiphase effects in a qualitative sense. Initially, experiments will be undertaken with glass beads. Later, we will move to geological materials that have oxidizable components capable of competing with chlorinated etheylenes for oxidation.

During the coming year, we will also begin to examine the possibilities for surface reactions and the possibilities for catalyzing oxidation reactions. We are presently working on the experimental design for this work.

Work is nearly complete on the validation of the code with experimental results from the literature. The next step with the modeling is a sensitivity analysis with the flow and transport model. The objective is to generalize the experimental results and to expand the understanding of reaction and transport mechanisms. This analysis will vary key parameters individually to study their effects on the redox processes.

Although this study is mainly oriented toward the characterization of various types of reaction pathways and geochemical processes, we expect that the approach would see eventual applications to site remediation. The modeling approach will be utilized in the study to provide testing schemes that would provide the next step forward in testing permanganate oxidation under field conditions. The eventual implementation could involve both reactive barrier systems (e.g., funnel and gate systems) or flooding for mass removal. Thus, we would develop appropriate tests for both types of potential applications.

Modeling of Cation Binding in Hydrated 2:1 Clay Minerals

David E. Smith, New Mexico State University

Research Objective

The primary focus of our research is the development of molecular theories of ion exchange on clay minerals, with a view toward understanding the mechanism of radionuclide transport through soils. The specific scientific goals of the study involve using molecular simulation methods to correlate clay-ion binding strengths with interlayer structure and swelling properties. This should build upon our fundamental understanding of clay behavior and allow for improvement in transport modeling of radionuclides in clay-rich soils

Research Progress and Implications

This report summarizes work after 1.75 years of a 3-year project.

Code Development: A computer simulation code for investigating hydrated smectite and vermiculite clays has been developed and validated. The code provides the ability to simulate clay minerals of varying composition (layer charge magnitude and location) and with either alkali or alkaline-earth interlayer ions. Simulations may be performed at fixed pressure or volume, and with either water content or water chemical potential held constant. A structure analysis module allows for a graphical display of average ion-clay binding geometries. Hydration (swelling) thermodynamics can be determined through calculations of isosteric adsorption energies, immersion energies, or P versus V data at fixed water chemical potential. The code also has the capability to calculate ion exchange free energies between like-valentions.

Hydrated Clay Structure: The molecular structures of Cs- and Na-montmorillonite have been determined as a function of clay water content and layer charge location. The observed layer spacings agree well with experimental swelling curves.[1] Analysis of calculated structures indicates that cesium preferentially forms inner-sphere complexes with the clay surface, except for ions located proximally to tetrahedral-layer substitution sites. Near these sites, both sodium and cesium ions are bound to the clay surface, with sodium residing above the substitution site and cesium occupying a hexagonal hole adjacent to the site. At other locations, cesium lies directly above the tetrahedral-layer silicon atoms.

Swelling Thermodynamics: Adsorption of cesium onto clay minerals is accompanied by dehydration, which in turn limits cesium diffusion.[2] Clay swelling should thus play an important role in both the thermodynamics and kinetics of ion binding in soils. Experimental water adsorption isotherms indicate that Na-montmorillonites will form multilayer hydrates while Cs-montmorillonites swell maximally to a monolayer.[1] We have calculated immersion energy curves for a Na-montmorillonite and for two Cs-montmorillonites. The simulations reveal oscillatory behavior, indicating that a discrete rather than continuous swelling process is energetically favored out to several water monolayers. To our knowledge, these calculations provide unique evidence of the energetic origin of discrete swelling in clay minerals. The global immersion energy minimum occurs at a monolayer water content for all clays studied. For Cs-substituted clays, this is in agreement with the known swelling behavior. In contrast, the data for sodium are not consistent with the expected formation of multilayer hydrates. This suggests that entropic effects also play a significant role in determining swelling extent in clays.

Monovalent Ion Exchange: Monovalent ion exchange calculations are being performed in two steps, with the first step involving ion mutation at fixed volume and water content, and the second

using constant water chemical potential methods to determine the swelling contribution to the exchange free energy. We have completed Na to Cs mutation calculations for a montmorillonite clay at several water contents. Calculations of the swelling contributions to the exchange process are presently underway. It is known that sodium is favorably exchanged with cesium on most clay minerals.[3] Our results for the monolayer hydrate (at fixed water content) show favorable exchange free energies for ions associated with octahedral layer charges. In contrast, simulations predict an incorrect, unfavorable exchange for ions associated with tetrahedral layer charges. This result may indicate a model flaw at the tetrahedral substitution sites. The exchange free energy for the two-layer hydrate is larger than for the monolayer hydrate by about 2 kcal mol^{-1}. This indicates correctly that Na-montmorillonite swells more readily than Cs-montmorillonite, and that the swelling contribution to ion exchange is significant. The decomposition of exchange free energies into 'mutation' and 'swelling' contributions is a unique and potentially powerful feature of the simulation approach used in this project.

Planned Activities

Improvement in the current model representation of tetrahedral substitution sites will be addressed (next 3 months) with density functional theory methods via collaboration with Dr. Randy Cygan (Sandia). A grand canonical molecular dynamics method[4] will be applied (next 3 months) in order to improve efficiency of the swelling calculations.

Calculations of monovalent ion exchange free energies for several clay compositions should be completed shortly (6 months), allowing for comparison of data with existing exchange theories. Investigations of Sr-substituted clay structure, swelling, and exchange will be initiated within 1 month and performed over the duration of the project period. A 'uranium phase' of the project will also be addressed in the final year of the project.

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Kinetics and Mechanisms of Metal Retention/Release in Geochemical Processes in Soil

Robert W. Taylor, Alabama A&M University

Research Objective

The long-term fate of toxic metals in soils cannot be precisely predicted, and often remediation recommendations and techniques may be ineffective or unnecessary. This work will generate basic knowledge on the kinetics and mechanism(s) of heavy metal retention/release by soil mineral colloids.

The information should assist in improving remediation strategies for toxic heavy metal contaminated soils. The objectives are:

1. To determine the effects of residence time on the mechanisms of Cr(VI), Cu(II), Co(II), Cd(II), Pb(II), and Ni(II) sorption/release on Fe and Al oxide and clay mineral surfaces using kinetic studies coupled to extended x-ray absorption fine structure (EXAFS) spectroscopy and fourier transform infrared (FTIR) spectroscopy.
2. To study the effect of temperature, pH, and phosphate on metal sorption by oxides, and derive thermodynamic parameters to describe the sorption process.

Research Progress and Implications

As of June, 16, 1997 several clay minerals were tested for their efficiency of removing Cr from aqueous systems. The materials tested - smectite, vermiculites, illites, and kaolinite - represent the natural clay minerals that are abundant in soils and sediments. The clays were used in either their original or reduced (reduced with sodium dithionite) forms. The experimental result indicate that the reduced clays acted as an efficient remover of Cr(VI) from an aqueous system. The XANES spectra of Cr-treated clays provided evidence that the clays reduced Cr(VI) to Cr(III) and immobilized Cr in the clays at the same time. Sodium dithionite applied directly into aqueous systems reduced Cr(VI) to Cr(III), but could not immobilize Cr even in the presence of the clays. The Cr(VI) removal capacity varied with the clay mineral type and the structural Fe content. For the clays used in this study, the removal capacity follows the orders of smectites>vermiculites and illites>kaolinite. Within the same type of clay minerals, reduction of Cr(VI) is highly related to the ferrous iron content of the clays, which indicates that the reduction of Cr(VI) to Cr(III) results from the oxidation of structural Fe(II) to Fe(III). The results of this study can be used to develop a method for remediation of chromium in waste water.

The mechanisms and conditions for coupled reduction-sorption of chromate in dithionite-reduced smectites was investigated in this study by both equilibrium and spectroscopic methods. The batch study showed that the maximum removal of Cr(VI) by the reduced smectite was highly related to its structural Fe(II) content. The surface cation type and ion strength which affected the expanding of smectite also influenced the electron transfer, and thus the coupled reduction-sorption processes. The pH of the aqueous system was a determining factor for both the amount of Cr(VI) reduced to Cr(III) and the partition of Cr(III) between aqueous and adsorbed species. The environments of chromium in the smectite were studied with various spectroscopies (IR, XRD, XANES, and EXAFS).

Our XANES projects are most heavily concentrated on two areas. The first is a study of chromium redox chemistry on contaminated soils. In this project we began collecting data on coupling between Cr(VI) reduction and Fe(II) oxidation and coupling between Cr(III) oxidation and Mn(IV) reduction in April 1998. The samples we are examining come from an eight-month experiment in incubated soils. A component of this study examines reactions between soil humic substances and Cr(VI), seeking to verify whether humic thiol groups act as reducing agents. Results collected in April confirm this, showing reductions in both thiol and thiophene groups accompanied with increases in sulfate (as expected) and sulfonate (unexpected). The transfer of electrons between reduced organosulfur groups to oxidized organosulfur groups exceeded the number of electrons needed to completely reduce Cr(VI). One series of proposed experiments will continue this investigation to determine organosulfur reactants and products. The redox chemistry of organosulfur groups in humic substances is part of an expanding program studying the chemistry of humic organosulfur groups. The proposed XANES studies at the S K-edge will allow us to quantify humic thiol ligands, essential data for the study of thiol complexation of chalcophilic (sulfur-loving) metals such as Hg(II) and Ag(I). We recently submitted a paper to Environmental Science & Technology reporting evidence that Hg(II) is coordinated by thiol and disulfide groups from humic substances, a finding of great interest to environmental chemists studying mercury chemistry in the environment. In collaboration with M. B. McBride (Cornell) we plan to study toxic metal chemistry and its relation to organosulfur in soils where municipal sewage sludge was disposed.

Planned Activities

The studies planned for Summer 1998 will examine the coupling of Cr reduction and oxidation to iron and manganese in soil. One series of experiments will study the reduction of soluble Cr(VI) by Fe(II) within the structure of layer silicate minerals. This study will determine changes in solution conditions influencing the reactivity of Fe(II) locked within silicate materials. The second series of experiments will collect Cr, Mn, and Fe K-edge XANES from soils contaminated with Cr(VI) and later treated by additions of soluble Fe(II) to promote reduction and Mn(IV) oxide minerals to promote re-oxidation of Cr(III) back to the toxic Cr(VI) form. The proposed XANES studies for Fall 1998 will concentrate the K-edges of two elements: S and Cr. These studies will examine electron transfer reactions involving organosulfur structures in humic substances and chromium in contaminated soils.

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Sorption of Colloids, Organics, and Metals onto Gas-Water Interfaces: Transport Mechanisms and Potential Remediation Technology

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Research Objective

Although contaminant sorption at mineral surfaces has received much recognition as a major mechanism controlling contaminant behavior in subsurface environments, virtually no attention has been given to the possibility of contaminant sorption at gas-water interfaces. Moreover, no effort has yet been advanced to optimize such interactions for the purpose of facilitating in-situ remediation. Gas-water interfaces, unlike water-solid interfaces, are mobile. Therefore, associations of contaminants with gas-water interfaces can be very important not only in subsurface contaminant distributions, but also in contaminant transport, and potentially in remediation. The first objective of this research is to develop a quantitative understanding of interactions between contaminants and gas-water interfaces. The anticipated results will provide insights into the poorly understood phenomenon of contaminant interactions with the gas-water interface, and improve our current conceptual models of contaminant behavior in subsurface environments. The second purpose of this research is to explore the possibility of using surfactant stabilized microbubbles for in-situ remediation. Both pump-and-treat, and air sparging remediation methods are ineffective at displacing contaminants in zones which are "advectively inaccessible". Stable microbubbles can migrate beyond preferential flow pathways and enter lower permeability zones by buoyant rise. The microbubbles can deliver oxygen and nutrients for promoting aerobic degradation of organic contaminants, and also deliver surfactants for emulsifying NAPLs.

Research Progress and Implications

This report summarizes work after 1.5 year of the 3-year project. In pursuing the first objective, significant results has been obtained. Previous researchers have qualitatively shown enrichment of colloids and colloid-associated heavy metals and organic compounds at the surface of oceans and lakes (which controls mass transfer between ocean and atmosphere), in subsurface vadose zones, and in engineered systems. For surface active molecules, changes in surface tension along with changes in solution concentration determine their surface excesses through the Gibbs equation. However, for suspensions of colloids, surface tension changes are often not measurable. Until initiation of this research project, there were no techniques for quantitatively measuring surface excesses of colloids at gas-water interfaces. In this project a simple bubble column method was developed to quantify surface excesses of colloids and colloids-associated molecules at air-water interfaces. In the bubble column, gas is bubbled through a vertical column containing the dilute aqueous suspension (or solution) of the colloids (or solutes). The rising bubbles sorb and carry the surface-active species upwards, then release them back to the solution at the free surface where the bubbles burst. At steady-state, a concentration profile is established along the column length which reflects the balance between upward transport by partitioning onto rising bubbles and downward transport by eddy dispersion. By directly measuring the column eddy dispersion coefficient for given conditions (column dimensions, air flow rate and bubble size) and measuring the steady-state concentration profile, the (interface-bulk) partition coefficient K, can be determined. To test the bubble column method, the adsorption isotherm constant of sodium dodecyl benzene sulfate (SDBS) obtained with the bubble column method was compared with the value obtained by conventional surface tension measurements. The K value of 64 ±4 μm for the SDBS obtained with the bubble column method is in good agreement with the K (64 ±12 μm) obtained from surface tension measurements. This agreement validated the bubble column technique as a method for determining partitioning of surface-active components at air-water interfaces. The bubble column method is also sensitive enough to quantify surface exclusion of colloids (negative K values), another very important capability of this method. The very first measurements of surface partition coefficients of two common types of colloids, clay and humic acid (HA) were conducted with the bubble column technique. The soil humic acid (1S102H, International Humic Substances Society) was used at concentrations of 4, 10, and 20 mg L-1, in 5 mM Na_2SO_4 at pH 6. The reproducible measurements of HA concentration profiles resulted a K value of 18 μm. A systematic study of different types of clay colloids at different pH and ionic strength conditions is still in progress. The initial results indicate that both kaolinite and montmorillonite can have very high surface partition coefficients under certain chemistry conditions, and that kaolinite generally partitions at the air-water interface much more strongly than montmorillonite. The solution conditions of pH 4.0-6.3, and ionic strength * 1.0 mM are most favorable for partitioning of these clays at the air-water interface. An article describing this work has just been accepted by the journal Environmental Science and Technology. An anonymous reviewer wrote: “This work makes significant contributions to the field of colloidal science, environmental fate and transport, and environmental remediation engineering. The theory and procedures are immediately accessible, repeatable, and to some extent verifiable.”

In pursuing the second objective, we have successfully employed previously developed techniques for generating microbubbles, identified suitable new surfactant combinations, optimizing stability of microbubble suspensions, and testing microbubble transport properties through porous media. Microbubble suspensions were generated by mixing a non-water soluble surfactant (Span 60) with a water soluble surfactant (e.g. SDS and Dowfax 8390) using a spinning disk technique. The disk (rotating at 10,000 rpm) produces strong waves on the surface of the aqueous suspension/solution of a combination of non-soluble and soluble surfactants, entrain air/oxygen into the liquid, and the entrained gas subsequently disperses into microbubbles. A microbubble is composed of a gas phase and a shell consisting of Span 60 particles and dissolved surfactant. The sizes of these microbubbles range from less than 1 μm up to 20 μm. Typical concentrations of these microbubble suspensions range up to 109 microbubbles per mL (determined by Coulter Multisizer). Stabilities of the microbubbles as functions of time and dilution were determined. Non-diluted SDS/Span 60 microbubbles were stable for up to seven weeks. The same results were observed for 1/10 dilution in

a solution of 1 mM NaCl + 0.5 mM $CaSO_4$. For 1/100 dilution the bubbles were stable up to 19 days. The stability of the microbubbles as a function of hydrostatic pressure was also investigated, revealing that pressures in small excess of atmospheric pressure can readily dissolve microbubbles. This indicates that underground injection of the microbubbles generated using our current approach will not be efficient. We are now testing a method to generate microbubbles under controlled higher pressures in order to increase the dissolved and microbubble-contained oxygen concentrations, and improve the pressure-stability of the microbubbles. The breakthrough curves of microbubble suspensions were measured through columns (25 cm long and 2.5 cm ID) packed with sand (250-425 μm), at flow rates ranging from 0.06 to 6 m/d. These preliminary tests showed slight microbubble retardation, and about 90% microbubble recovery. If the aforementioned pressure stability problem is resolved, we expect that microbubble injection will be useful in certain remediation efforts where it is desirable to deliver oxygen, nutrients, and surfactants to the subsurface, including advectively less accessible zones.

Planned Activities

1. Complete studies on clay colloids in ideal "clean" systems.
2. Study air-water interface behavior of clays sorted from vadose zone samples (from DOE contaminated sites such as Hanford).
3. Study partitioning of iron oxyhydroxide colloids in both "clean" and contaminated systems.
4. Study partitioning in more complexed systems containing mixtures of heavy metals, natural organic matter, and organic contaminants.
5. Continue to develop the microbubble remediation technique.

The Efficacy of Oxidative Coupling for Promoting In-Situ Immobilization of Hydroxylated Aromatics in Contaminated Soil and Sediment Systems

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Research Objective

Hydroxylated aromatic compounds (HAC's) and their precursors are common contaminants of surface and subsurface systems at DOE facilities. The environmental fate and transport of such compounds, particularly in subsurface systems, is generally dominated by their sorption and desorption by soils and sediments. Certain secondary chemical reactions, most specifically abiotic and/or enzymatic oxidative coupling, may be significant in controlling the sorption and subsequent desorption of such hydroxylated aromatics by soils and sediments. The principal objectives of this study are to investigate: 1) the role of abiotic/enzymatic coupling reactions on the immobilization of HAC's; 2) the effects of environmental factors on such immobilization; and 3) preliminary engineering approaches utilizing enhanced abiotic/enzymatic coupling reactions to immobilize hydroxylated aromatics in-situ. Information gathered from the study will be useful in quantifying the behavior of this class of organic

compounds in various subsurface contamination scenarios relevant to DOE facilities, and in specifying strategies for the selection and design of remediation technologies.

Research Progress and Implications

Over the first two years of this three-year project, we have developed a significantly improved understanding of the mechanisms of hydroxylated aromatic compound sorption and immobilization by natural soils and sediments. Immobilization in this context is attributed to oxidative coupling of the hydroxylated aromatics subsequent to their sorption to a soil or sediment, and is quantified in terms of the amount of a sorbed target compound retained by a sorbent after a series of sequential water and solvent extractions. The presence of oxygen, metal oxides, and organic matter, all of which can potentially catalyze/facilitate the abiotic oxidative coupling of HAC's [1], were investigated during these first two years. Three different HAC's: phenol, trichlorophenol and *o*-cresol were included in the experimental program. Inorganic soil matrices were represented by a glacial wash sand (Wurtsmith sand) having very low organic content. Because the chemical nature of soil organic matter may potentially affect the extent of coupling or immobilization [2], sorbents having different organic matter compositions are being investigated. Two of the three studied to date are near-surface soils, characterized by geologically younger organic material (Fox Forest soil and Fox Grassland soil). The third sorbent is an older and diagenetically altered soil (Lachine Shale). Sorbent preparation, characterization and experimental protocol development were completed in the first year of the study while the second year of the project has focused primarily on experiments with natural systems, as planned. Preliminary work with engineered systems has been initiated earlier than scheduled in order to integrate and relate all aspects of the study.

Three different experimental approaches were used to demonstrate the occurrence of oxidative coupling in the immobilization of the HAC's: 1) determination of extractable and non-extractable fractions of the contaminant, 2) comparison of oxic/anoxic isotherms, and 3) evaluation of sorption/desorption hysteresis indices. Our initial hypothesis that soils and sediments having organic matter comprised of geologically younger organic materials are more likely to have potential for immobilization of hydroxylated aromatic contaminants is supported by the experimental results. As presented in Fig.1, up to 75 % of sorbed phenol is immobilized by Fox Forest Soil. A similar trend was observed for the Fox Grassland Soil. In contrast, diagenetically altered materials such as Lachine Shale, although having higher sorption capacity and higher total iron concentration did not promote phenol immobilization (Fig. 2).

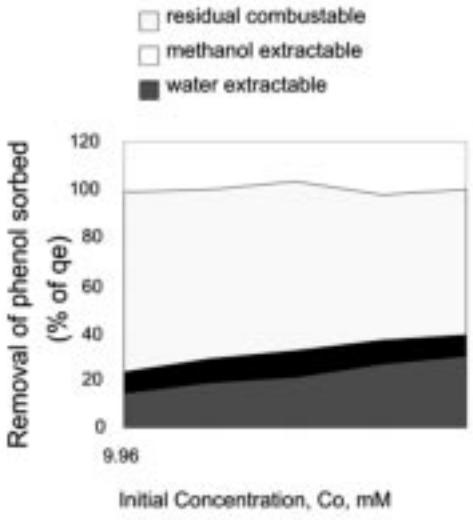

Figure 1 Distribution of phenol sorbed by Fox Forest Soil.

Sorption/Desorption experiments were conducted under oxic/anoxic conditions to verify the hypothesis that oxidative coupling and contaminant immobilization can be induced by the presence of oxygen in subsurface systems (Fig. 3). If oxidative coupling is the primary mechanism, we can expect a difference in sorption behavior under these two different conditions. Indeed, it was demonstrated that the significant immobilization observed for phenol on Fox Forest soil (Fig. 1) translated into detectable differences between its oxic and anoxic isotherms (Fig. 3). Conversely, for the soil for which no significant immobilization was observed (Fig. 2), there was no significant difference in the oxic and anoxic isotherms.

Iron and manganese oxides have been known to catalyze the oxidative coupling of HAC's [3]. Preliminary work with the four natural sorbents described above revealed, however, that total iron and manganese contents are not good predictors of immobilization. This suggests that the oxidative state or/and crystal structure of the metal oxides might be important. Detailed characterization of metal oxides associated with various soils will be performed as a part of the on going study.

One generally accepted method of quantifying irreversible sequestration of solutes by adsorbents is to measure aqueous phase sorption/desorption hysteresis and express the results in terms of a hysteresis index (H.I.) [4]. As demonstrated in Fig. 4, for the systems studied to date, several types of

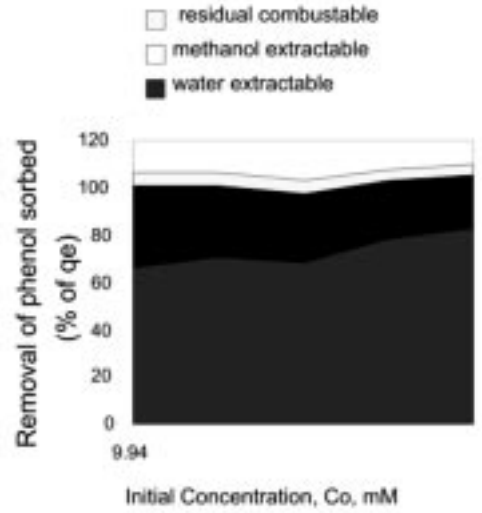

Figure 2 Distribution of phenol sorbed by Lachine Soil.

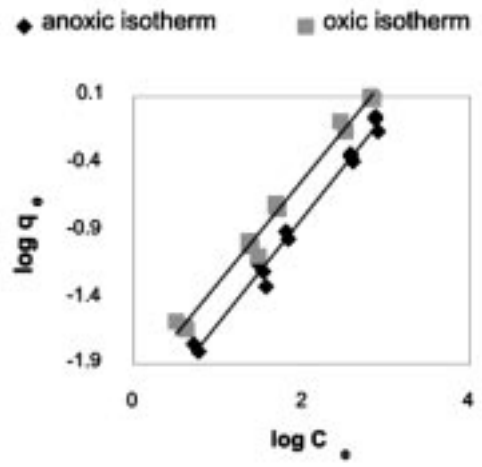

Figure 3 Oxic/anoxic isotherm of phenol sorption on Fox Forest soil.

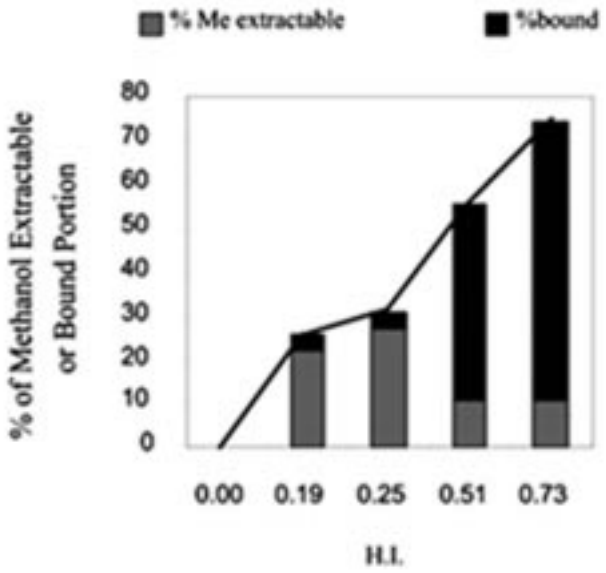

Figure 4 Sources for phenol sorption on Lachine Shale, Forest and Grassland Soils (H.I. = 0.19, 0.73, and 0.51, respectively) and 0-cresol sorption on Lachine Shale (H.I. = 0.25).

interactions appear to be responsible for the hysteresis observed. For low values of H.I. both hydrophobic interactions and hydrogen bonding appear to be important contributors (solvent extractable fraction). However, for high values of H.I immobilization by oxidative coupling dominates.

Planned Activities

Pursuant to the project schedule, all work associated with the model (Phase II) and engineered (Phase III) systems will be completed. Phase II includes evaluation of the efficiency of immobilized enzymes and transition metal oxides in promoting oxidative polymerization of the target hydroxylated aromatics compounds. Phase III involves addition of immobilized enzymes, metal oxides, and possibly organic matter to the four selected natural sorbents to evaluate the efficacy of oxidative coupling induction. Immobilization of the three HAC's in these amended soil systems will be also evaluated in a flow-through multi-port column systems. This will simulate in-situ applications of the research in reactive wall configurations.

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

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Research Objective

Cesium (137) is a major component of high level weapons waste. At Hanford, single shell tanks (SST's) with high level wastes (HLW) have leaked supernate containing over 10^6 Ci of ^{137}Cs and other co-contaminants into the vadose zone. In select locations, ^{137}Cs has migrated further than expected from retardation experiments and performance assessment calculations. Deep ^{137}Cs migration has been observed beneath the SX tank farm at Hanford with REDOX wastes as the carrier causing regulatory and stakeholder concern. The causes for "expedited" migration are unclear.

This research is investigating how the sorption chemistry of Cs on Hanford vadose zone sediments changes after contact with solutions characteristic of HLW. Our central scientific hypothesis is that the high Na concentration of HLW will suppress surface-exchange reactions of Cs, except those to highly-selective frayed edge sites (FES) of the micaceous fraction. We further speculate that the concentrations, ion selectivity, and structural aspects of the FES will change after contact with HLW and that these changes will be manifest in the macroscopic sorption behavior of Cs. We believe that migration predictions of Cs can be improved substantially if such changes are understood and quantified.

The research has three objectives:

1.) Identify how the multi-component surface exchange behavior of Cs on Hanford sediments changes after contact with HLW simulants that span a range of relevant chemical (Na, OH, Al, K) and temperature conditions (23-80^0 C).
2.) Reconcile changes in sorption chemistry with microscopic and molecular changes in site distribution, chemistry, mineralogy, and surface structure of the micaceous fraction.
3.) Integrate mass-action-solution exchange measurements with changes in the structure/site distribution of the micaceous fraction to yield a multicomponent exchange model relevant to high ionic strength and hydroxide for prediction of environmental Cs sorption.

Research Progress and Implications

The project was initiated in September 1997. Since that date, research has investigated 1.) the mineralogic residence and speciation of ^{137}Cs in contaminated materials collected from beneath SST SX-109 at Hanford and 2.) the Cs ion exchange characteristics of a mica-containing composite sediment from the Hanford formation.

^{137}Cs Contaminated Materials - Three samples were obtained from the upper levels of Hanford borehole SX-41-09-39 in December 1997 that each contained in excess of 10^4 pCi/g ^{137}Cs. The coring was an EM supported activity that extended the borehole beneath SX-109 from 39.6 m to 5 m below groundwater (at 65 m) to define contaminant distribution in the vadose zone. Our objective in studying these materials was to confirm the hypothesized ^{137}Cs-mica association in sediments contacted by HLW.

- Contaminated sediments were size fractionated and counted. The highest activity was observed in the coarse sand fraction, but greater than 60% of total radioactivity was observed in the silt and clay. The adsorbed ^{137}Cs was not readily desorbed by Na.
- The mineralogy of the ^{137}Cs-containing size fractions was evaluated by X-ray diffraction (XRD), and mica comprised 15-20% of the materials on a mass basis. Three distinct mica types were observed: muscovite, biotite, and vermiculitized biotite.
- ^{137}Cs occupied less than 1% of the ion exchange capacity of the sediment, the remainder was comprised of Na^+ and K^+.
- Individual ^{137}Cs containing particles were isolated and are being characterized by single-particle XRD and TEM. Preliminary data indicates they are micaceous in composition.

Cs Sorption Chemistry on Hanford Vadose Zone Sediments - A bulk sediment (20 kg) sample representative of the 15-40 m depth interval at Hanford was established by compositing core subsamples from six RCRA wells placed around the uncontaminated periphery of the SX tank farm in the Hanford 200 West Area. Particle size distribution, mineralogy, chemical composition, cation exchange capacity with different index ions, and surface area have been measured on the composite sediment. Cs interaction experiments have been performed with the sediment as a precursor to ion exchange thermodynamic studies and contact experiments with HLW simulants. Key findings are as follows.

- Cs^+ sorbs rapidly to Hanford sediments by ion exchange. Cs^+ fixation by the micaceous component occurs slowly, but little Cs^+ desorption can be initiated by K^+ at 100-fold excess after contact periods of a month or more.
- Highly selective FES exist in the Hanford sediments and these represent < 0.1 % of the cation exchange capacity. The FES themselves exhibit great variation in their selectivity for Cs^+. Distribution coefficients on the FES range from $10\text{-}10^4$, and are strongly influenced by other cation concentrations.
- As hypothesized, high salt (Na^+) suppresses all Cs^+ sorption except that to FES. An increase in Na^+ concentration from 5 mol/L to $NaNO^3$ saturation (9 mol/L), however, induces further reductions to Cs sorption indicating that competitive ion exchange of Cs^+ and Na^+ occurs on the FES.

Implication - Our Cs^+ sorption measurements in saturated $NaNO_3$ are the first reported at such high Na^+ concentration. Sodium exhibits a mass action suppression on Cs^+ sorption from dilute concentration to saturation. Our preliminary measurements suggest that high Na^+, alone, may cause expedited Cs^+ migration below leaking tanks with salt cake (e.g., REDOX), although other effects resulting from high OH and $Al(OH)_4$ are also expected.

Planned Activities

Remaining FY 98 research will complete experiments and modeling for two manuscripts: one on the mineralogic residence and desorbability of ^{137}Cs in contaminated Hanford vadose zone sediments, and the other on Cs sorption thermodynamics and kinetics in the composite sediment. FY 99 activities will focus on the impacts of high base, variable temperature induced mineral dissolution on Cs^+ sorption in Hanford sediments and isolated mica fractions. We will determine whether the selectivity of the mica fraction for Cs^+ is changed by molar concentrations of hydroxide, and whether changes result from competitive ion effects (e.g., K^+ release by dissolution) or structural destabilization of the FES. The latter issue will be resolved by using p scanning probe microscopy, high resolution transmission electron microscopy, and X-ray absorption spectroscopy. FY 00 studies will focus on high-base waste simulants containing $Al(OH)_4^-$. At issue is whether $Al(OH)_4^-$ precipitation that follows base neutralization will change Cs^+ sorption selectivity, kinetics, and reversibility. Important questions to be resolved include the nature of the precipitated Al-phase and whether it causes hydroxy pillaring and alteration of the structural environment of the FES. A combination of microscopy, solution phase thermodynamic measurements, and chemical modeling will be employed to interpret results and resolve hypotheses.

A Hybrid Hydrologic-Geophysical Inverse Technique for the Assessment and Monitoring of Leachates in the Vadose Zone

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T. C. Yeh, University of Arizona
Douglas LaBrecque, Steamtech Environmental Services, Inc.

Research Objective

The objective of this study is to develop and field test a new, integrated Hybrid Hydrologic-Geophysical Inverse Technique (HHGIT) for characterization of the vadose zone at contaminated sites. This new approach to site characterization and monitoring can provide detailed maps of hydrogeological heterogeneity and the extent of contamination by combining information from electric resistivity tomography (ERT) surveys, statistical information about heterogeneity and hydrologic processes, and sparse hydrologic data. Because the electrical conductivity of the vadose zone (from the ERT measurements) can be correlated to the fluid saturation and/or contaminant concentration, the hydrologic and geophysical measurements are related.

Research Progress and Implications

As of the 21st month of a 36-month project, a three-dimensional stochastic hydrologic inverse model for heterogeneous vadose zones has been developed. This model employs pressure and moisture content measurements under both transient and steady flow conditions to estimate unsaturated hydraulic parameters. In this model, an innovative approach to sequentially condition the estimate using temporal measurements has been incorporated. This allows us to use vast amounts of pressure and moisture content information measured at different times while keeping the computational effort manageable.

Using this model we have found that the relative importance of the pressure and moisture content measurements in defining the different vadose zone parameters depends on whether the soil is wet or dry. We have also learned that pressure and moisture content measurements collected during steady state flow provide the best characterization of heterogeneity compared to other types of hydrologic data. These findings provide important guidance to the design of sampling scheme of the field experiment described below.

To provide images from ERT data that includes the same statistical information as the hydrologic inverse model, a new stochastic ERT inversion code has been written and tested. During testing, we found that the basic stochastic assumptions used to construct the solution provide poor results. We believe the problem lies in the assumption that the mean and variance of the electrical conductivity are stationary across the region of interest. Two different methods have been incorporated to improve the solution: 1) the a-priori variance is increased in the center of the image region where the sensitivity is small, and 2) the inversion process is initialized with a starting model that is derived by Kriging apparent resistivity values calculated from ERT measurements made between adjacent electrodes.

A study comparing surveys where data were collected with different electrode configurations has been completed. Surprisingly, pole-pole surveys provided improved resolution over dipole-dipole surveys. Also, increasing the number of surface electrodes substantially improved image quality. Because surface electrodes are generally less expensive to implement than borehole electrodes, increasing the number of surface electrodes decreases the number of boreholes needed to monitor a volume, thus reducing implementation costs. These results are being applied to design ERT surveys proposed at a number of DOE sites.

The construction of a test site at which data will be collected to test the HHGIT method is nearing completion. The Sandia-Tech Vadose Zone Infiltration Test Site (STVZITS) is located adjacent to the New Mexico Tech campus in Socorro, New Mexico, on highly permeable ancestral Rio Grande sands and gravels. Facilities and instrumentation have been designed and constructed to provide a long-term research facility.

An infiltration system, to be located at the center of the instrumented site, has been designed to produce a constant flux boundary condition across a 3m by 3m infiltration pad. Thirteen wells cased with PVC provide subsurface access for neutron moisture probes as well as other geophysical devices; sixteen wells for nests of tensiometers; and four wells for time domain reflectometry (TDR) probes grouped with tensiometers, suction lysimeters, and thermocouples, have been emplaced axi-symmetrically about the center of the infiltration pad. The location and depths of these sensors has been determined partly from the aforementioned hydrological simulations as well as the characterization process described below. Eight vertically installed ERT electrode strings and a grid of 36 surface electrodes have also been installed at the site. Each string contains 17 electrodes ranging in depth from the surface to a depth of 12m depth. The ERT electrodes are also arranged axi-symmetrically about the infiltration pad. A three-channel ERT data acquisition system has been built and tested. Background data set has been collected and the data is being processed. All data collection systems are contained in a building immediately adjacent to the experimental pad.

The site has been characterized geologically, hydrologically and geophysically. Geological characterization consisted of drillers logs, and measurements of bulk density and grain size distributions on samples that were collected during drilling and trenching. Hydrologic characterization consists of measurements of hydrologic sensors and neutron tubes prior to the beginning of the infiltration, and laboratory measurements of samples collected during drilling. These measurements include pressure versus saturation, saturated hydraulic conductivity and electrical resistivity at different water saturations.

In addition to the baseline ERT measurements, cross well GPR, conductivity and natural gamma well logs made between and within the PVC cased wells have been employed successfully to geophysically characterize the site (other methods including surface GPR and TEM have been attempted with less success). The different characterization techniques all show approximately 5m of interbedded sands, silts, clays and gravels of moderate saturation overlying 7m of fairly low clay, semi-homogenous drier sands.

Planned Activities

In the coming months, we will be developing a maximum likelihood algorithm to estimate the statistical structure of heterogeneity which is one of the input parameters to our inverse models. We will then assess the effect of uncertainty associated with this structure. A Newton-Raphson iterative solution will be implemented in the forward hydrologic model to improve the solution for highly nonlinear problems. We will also begin integrating the stochastic ERT code with the hydrological codes. In the near term (this summer) this involves performing a cooperative inversion in which moisture information derived from the hydrological models will be converted to resistivity data via co-Krieging to improve the ERT inversion, and vice versa. During the fall and winter, the two routines will be coupled together into a full joint ERT/hydrological inversion routine.

Starting in mid to late June, water infiltration will begin at the STVZTS. ERT and hydrologic data will be collected daily during the two or three weeks after starting infiltration, and less frequently afterwards as the system approaches steady state. After steady state has been reached, a salt pulse will be introduced to study contaminant transport in unsaturated yet steady state conditions. This fall a slope adjacent to the test site will be excavated to provide samples for the continued geologic, hydrologic and geophysical characterization. From these samples we will determine if it is possible to estimate saturated hydraulic conductivity from bulk density and grain size distribution measurements.

Inversions will be made both on the full ERT and hydrologic data sets as well as subsets of the data as the data become available. The results of these inversions will be compared to borehole geophysical logs (conductivity and neutron) and with cross-borehole GPR surveys. We will also investigate converting the velocity images obtained with the GPR to images of moisture content via Topp's equation as a possible additional source of geophysically derived hydrologic information.

Joint Inversion of Geophysical Data for Site Characterization and Restoration Monitoring

Patricia A. Berge, Lawrence Livermore National Laboratory

Jeffery J. Roberts, Lawrence Livermore National Laboratory
James G. Berryman, Lawrence Livermore National Laboratory
Dorthe Wildenschild, Lawrence Livermore National Laboratory

Research Objective

The purpose of this project is to develop a computer code for joint inversion of seismic and electrical data, to improve underground imaging for site characterization and remediation monitoring. The computer code developed in this project will invert geophysical data to obtain direct estimates of porosity and saturation underground, rather than inverting for seismic velocity and electrical resistivity or other geophysical properties. This is intended to be a significant improvement in the state-of-the-art of underground imaging, since interpretation of data collected at a contaminated site would become much less subjective. Potential users include DOE scientists and engineers responsible for characterizing contaminated sites and monitoring remediation of contaminated sites. In this three-year project, we use a multi-phase approach consisting of theoretical and numerical code development, laboratory investigations, testing on available laboratory and borehole geophysics data sets, and a controlled field experiment, to develop practical tools for joint electrical and seismic data interpretation.

Research Progress and Implications

This report summarizes work after about 1.7 years of a 3-year project. Progress on laboratory measurements is described first, followed by progress on developing algorithms for the inversion code to relate geophysical data to porosity and saturation.

Since limited information is available for unconsolidated sediments at low pressures appropriate for the near-surface, particularly for sediments containing clays, we have made our own laboratory measurements for unconsolidated sand-clay mixtures and are in the process of reducing and interpreting both elastic and electrical properties data. We have been conducting a series of electrical and elastic properties measurements on sand-clay mixtures containing 0%, 3%, and 10% clay, using filtered, deionized water, tap water, and $CaCl_2$ brines having a range of different salinities for the saturating fluids. The conductivity of the solutions ranged from about 0.002 mS/cm to 64 mS/cm. Fully saturated samples were used for electrical conductivity measurements. Dry and fully saturated samples were used for the velocity measurements since partial saturation introduces a significant degree of complexity to the problem. We have been investigating the effects of different clays such as kaolinite, bentonite, and a natural clay-rich soil called Alligator clay. We have used various mixing techniques to construct the sand-clay samples, since the microgeometry is a critical factor affecting measured elastic and electrical properties. We measured porosities and permeabilities as well as geophysical properties. This provides the needed information for developing relationships between geophysical properties and the hydrogeologic parameters that are most useful for environmental applications. Our laboratory measurement results suggest that microstructure controls the geophysical properties. Thus microstructure assumptions used in empirical or theoretical methods may be the determining factor for which methods are most successful in relating geophysical properties to porosity and saturation.

The results of velocity measurements on samples containing swelling clays are described in the Bonner et al. (1997) reference listed in the Additional Information section of the Web version of this report. The major implication of these results is that the wave amplitudes are critical data, as well as the wave velocities, and that the vadose zone may have more complex behavior than deeper regions.

Results of electrical conductivity measurements showed that the bulk sample conductivity ranged from approximately 0.023 to 14.3 mS/cm for pure sand; 0.1 to 6.4 mS/cm for 3% clay; and 0.4 to 3.5 mS/cm for 10% clay. The bulk sample conductivity varies linearly with the fluid conductivity according to the equation

$$sbulk = sfluid/F + 2Ss/LF$$

where F is the formation factor, Ss the surface conductance, and L is a geometrical parameter related to dynamically connected pore sizes. Estimates of the formation factor F range from ~4.5 for the pure sand sample to ~12.8 for the 10% clay sample. More details on these results are in the Additional Information section of this report.

We are developing the necessary algorithms for the inversion code using a flexible approach that allows us to assess the relative usefulness of geostatistical methods, empirical techniques commonly used in borehole geophysics interpretation, and rock physics theories that describe how elastic wave velocities and electrical conductivities depend on porosity and saturation in porous materials having different microgeometries. For testing geostatistical methods, we have made an exhaustive search of the marine geophysics, civil engineering, soil mechanics, exploration geophysics, and environmental geophysics literature to find available information on rock properties measurements for unconsolidated sands and clays at low pressures (i.e. shallow depths). We have compiled a database containing elastic properties data for unconsolidated sediments that we are using to modify and test the necessary algorithms for relating elastic properties to porosity and saturation for dry and fully saturated sediments. We found that laboratory data for very low pressures appropriate to shallow depths (e.g., the top 50 m of the subsurface) are sparce and contain large amounts of uncertainty. Our own laboratory measurements greatly augment the available database for elastic properties, particularly since we were able to obtain reliable shear wave measurements at very low pressures. For the rock physics approach, we have selected theories that are appropriate for the microstructures typically found in shallow sediments, including the self-consistent theory developed by Berryman and theories that provide bounds on rock properties, particularly the lower bound for an unconsolidated medium. Additional work on effective medium theories is described in the Berryman and Pride (1997), Dvorkin et al. (1997), and Pride et al. (1998) References listed in the Additional Information section. Existing effective medium theory methods commonly used with consolidated materials at moderately high pressure conditions, such as the differential effective medium theory algorithm that Berge developed for modeling velocities of volcanic rocks and cemented sandstones, are not appropriate for application to the near surface environment. One early implication of our work is that codes typically used in the oil industry cannot be applied to environmental applications if they rely on theoretical methods such as the differential effective medium theory.

Planned Activities

The schedule of this project is as follows: In the first year, investigators perform laboratory measurements of elastic and electrical properties of sand-clay mixtures containing various fluids. Investigators also develop methods of relating measurable geophysical properties to porosity and saturation by using rock physics theories, geostatistical, and empirical techniques together with available laboratory measurements. In the second year, investigators finish any necessary laboratory measurements and apply the methods developed in the first year to invert available borehole log data to predict measured properties of cores and sediments from a borehole. Investigators refine the inversion code in the third year and carry out a field experiment to collect seismic and electrical data. Investigators then use the inversion code to invert the field data to produce estimates of porosity and saturation in the field area where the data were collected.

Other Access To Information

Additional Information

This section provides additional detail on the laboratory measurement results and a list of the publications that were produced as part of this EMSP project.

Additional Details of Laboratory Results

We found that small amounts (3%) of swelling clay affect the pressure (depth) dependence of elastic wave velocities at low pressures (below 0.1 MPa, i.e. top few m), and the ratio of amplitudes for compressional and shear waves depends on clay content even for small amounts of clay. Saturated samples behaved like mechanical suspensions, as expected. Experiments with imbibition and with drained samples showed that minor residual gas in saturated samples and residual fluid retained by the clay in a drained sample strongly affect wave amplitudes. We are working on determining the surface conductance term and L parameter for each sample. The surface conductance contribution is apparent in plots of log bulk sample conductivity versus log solution conductivity where two distinct regions are indicated: one where the log bulk sample conductivity is nearly independent of log solution conductivity (fluid conductivities less than ~ 1 mS/cm), and another region where the log sample conductivity varies directly with log fluid conductivity (fluid conductivities greater than ~1 mS/cm). We observe that the pure sand sample does not display the above described flat region indicating no surface conduction component exists in the absence of clay. The greater the clay content, the greater the surface conduction contribution to bulk sample conduction. Measurements are currently being performed on samples containing ~10% clay in layers or distributed as discrete domains as a test of effective medium models.

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Surface and Borehole Electromagnetic Imaging of Conducting Contaminant Plumes

James G. Berryman, Lawrence Livermore National Laboratory

Research Objective

Electromagnetic induction tomography is a promising new tool for imaging electrical conductivity variations in the earth. The source field is a magnetic field generated by currents in wire coils. This source field is normally produced in one borehole, while the received signals are the measured small changes in magnetic field in another, distant borehole; however, the method may also be used successfully in combination with surface sources and receivers. The goal of this procedure is to image electrical conductivity variations in the earth, much as x-ray tomography is used to image density variations through cross-sections of the body. Although field techniques have been developed

and applied to collection of such EM data, the algorithms for inverting the magnetic data to produce the desired images of electrical conductivity have not kept pace. The current state of the art in electromagnetic data inversion is based on the Born/Rytov approximation (requiring a low contrast assumption), or extensions. However, it is known that conductivity variations in fact range over several orders of magnitude and therefore require nonlinear analysis. The goal of this project is therefore to join theory and experiment to produce enhanced images of electrically conducting fluids underground, allowing better localization of contaminants and improved planning strategies for the subsequent remediation efforts.

Research Progress and Implications

Code Development

Since the transmitters in our field experiments are induction coils with alternating current at a fixed frequency (typically in the range 1-10 kHz), our basic numerical problem is to solve Maxwell's equations in the frequency domain. Because of the practical frequency ange (< 1 MHz), it is adequate to ignore displacement currents in the formulation as is ypically done by other researchers, but it is not essential to do so in the particular mplementation that we have chosen. We have used the finite-difference frequency-domain formulation and an anisotropic PML (perfectly matched layer) approach to oundary conditions to deal with the fact that the computations must be done in a finite omain even though the real problem is effectively of infinite domain. The resulting ormulas for the forward solver reduce to a problem of the form Ax = y, where A is a non- ermitian matrix with real values off the diagonal. The matrix A may be either symmetric r nonsymmetric depending on details of the boundary conditions chosen (i.e., the articular PML used in the application), but in our implementations we always try to make hoices resulting in symmetric matrices. The equation Ax=y must be solved for the vector which represents field quantities such as electric and magnetic fields) with the data vector etermined by the boundary conditions and transmitter location. There are many choices of forward solver for this system, but few of these have been thoroughly tested for the type of matrix encountered in our problem. We found the stability characteristics of the frequently used Bi-CG algorithm for solving Ax=y to be quite inadequate (in terms of both reliability and uniform accuracy) for our application and have chosen instead to use an alternative developed for such situations called Bi-CGSTAB. We have found the stability characteristics of the new solver to be entirely adequate for our application.

Considerable effort was devoted to finding good test cases for validating our new 3-D EM code. We have tested various cases against results found in the literature. One example is for receivers down a borehole in a layered medium with air above the free surface, a 60m thick layer with conductivity 0.3 S/m, a 25m thick layer with conductivity 0.016 S/m, and a 60m layer with conductivity 0.2 S/m at the bottom of the model, with appropriately designed PML absorbing layers on all six sides of the domain. Relative permittivity of all three earth layers is constant and assumed to equal 10.0. The frequency of the excitation is f = 1 kHz with the transmitter located at the free surface with an offset of 5m from the borehole. The finite difference representation was chosen so the unit spacing in the earth model was 2.5m, with 50 cells by 50 cells in the xy direction, and 10 layers of PML on all four sides. In the vertical direction, there were 68 cells in the earth model, 10 cells in the air above the free surface, and 10 more cells above and below for the PML layers.

All PML cells are 10m thick in the directions 70x70x100 ~= 500,000 cells. The computations were performed on a DEC Alpha 8400 Model 5/4400, and required approximately 2 hours of CPU time, including about 2000 iterations to achieve the desired convergence. This computation was serial and required about 500 MB of memory. The results of the code calculations for the magnetic field magnitude and phase have been compared to results for the same model obtained using the code EM1D based on a semianalytical formula for such layered models. The observed agreement is excellent. Further tests in two and three dimensions have been performed or are in progress.

A new approach to the inverse problem of electromagnetics is being developed based on the so-called "adjoint technique." This method has the very useful characteristic that the inverse problem can be solved approximately by making two uses of the same forward odeling code that we have already developed. The updates to the electrical conductivity are obtained by first making one pass

through the code using the latest best guess of the characteristics of the conducting medium. Then another pass is made with the adjoint operator (which for this problem is just the conjugate transpose of the operator A, and therefore for symmetric A changes only the sign of the imaginary part of the diagonal elements). Then the results of the two calculations are combined to determine the update to the original conductivity model.

Field Work and Data Interpretation

The improvements to the data acquisition system have been planned and implemented. improvements included: (1) additional data channels, (2) faster, more reliable software, (3) purchase and testing of three new magnetomaters for borehole and surface imaging work, and (4) securing a larger, newer, more reliable, safer data acquisition vehicle, and (5) a larger, newer, more reliable, safer boom/ logging truck. All these improvements are now essentially complete and the system was successfully field tested in April, 1998, during a cross-borehole data collection at Lost Hills, CA, an active oil field owned by Bakersfield Energy Company. The system worked well, and only minor changes should be necessary from now on.

The Lost Hills experiment had 500 transmitter positions in the borehole ranging in depth from 20 to 120 m. Transmitter polarization in the borehole was always vertical. (The data were later decimated to only 100 transmitter positions to eliminate redundant data.)

The receivers on the surface were placed at 18 locations ranging from 5 to 120 m in steps of either 5m (out to 60m) or 10m (beyond 60m) from the transmitter borehole. Two nearly orthogonal surface survey lines of this type were used, and both vertical and radial polarization data were collected for each line. Total data collection after decimation was therefore 18x2x2x100 = 7200 measurements. These field data from Lost Hills, CA, have een reduced and are currently being interpreted, and prepared for use in our inversion code.

Planned Activities

Code development is the main focus of the project in the near term as we need the inversion code to analyze the data already collected as well as for any new data we will collect. Further fields tests are planned. One field site which may present a good opportunity for field testing our system is the Southern California Edison pole yard at Visalia, CA, which is contaminated with creosote. This site is currently under steam remediation and is also being monitored using ERT (electrical resistance tomography). Other opportunities for field testing are also being explored. Two papers are currently in preparation, one on the computational aspects of forward modeling and another on the theoretical and computational aspects of the inversion methods. A third paper summarizing our field experience will follow.

Other Access To Information

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The Use of Dielectric and NMR Measurements to Determine the Pore-Scale Location of Organic Contaminants

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Research Objective

The objective of our three-year research project is to investigate the effect of adsorbed organics on the dielectric and nuclear magnetic resonance (NMR) response of porous geological materials. This will allow us to assess the use of dielectric and NMR measurements at a site to determine whether organic contaminants are present in the central volume of the pore space or are adsorbed to the solid surfaces. In addition, we propose to use laboratory dielectric and NMR measurements to study the kinetics of the adsorption and desorption of organics.

Research Progress and Implications

This report summarizes work completed after 20 months of a three-year project. Our research involves the study of the NMR and dielectric behavior of sands with three types of solid surfaces: water-wet, where water spontaneously coats and adsorbs to the solid surfaces; hydrophobic, where water is repelled from the solid surfaces by an organosilane coating; and oil-wet, where oil coats the solid surfaces. The oil-wet case is representative of a contaminated soil, in which oil has become adsorbed to the solid surfaces.

We have completed the development of reliable and re-produceable procedures for sample preparation for the NMR and dielectric measurements. Water-wet sand samples are prepared using either a natural quartz sand, reagent grade pure quartz sand or silica gel. These solids are sequentially rinsed in 10% HCl, 10% NaOH, and distilled water, then oven-dried, in order to remove impurities and homogenize their surfaces. Hydrophobic samples are prepared by reacting water-wet solids with 5% octadecyltrichlorosilane in toluene for 48 hours at 110°C. Oil-wet samples are prepared by exposing the hydrophobic samples to a suspension of crude oil in toluene-heptane-alcohol. In addition to the preparation of samples with a homogeneous surface, we have developed a procedure that allows us to control and monitor the amount of oil adsorbed to a water-wet surface. In this procedure, a known weight of water-wet solid is simultaneously exposed to an aqueous phase (0.01 M NaCl) and an organic phase (toluene-heptane) containing a known concentration of oil.

The key experimental variable in our experiments is the state of the solid/fluid interface. The size of the interface is equivalent to the surface area of the solid, which for the natural sand and pure quartz sand is approximately 1 m2/g, and for the silica gel is approximately 200 m2/g. As a means of characterizing the solid/fluid interface, we perform acid-base titrations to determine the magnitude of the electric charge at the solid surface, and its relation to the pH of the surrounding solution. The water-wet solids display roughly 2 x 10^{-6} equivalents of charge per m^2 surface area and are all positively charged below pH 2 and negatively charged above pH 2. The hydrophobic surfaces display acid-base behavior which indicates that there is essentially no electric charge at the hydrophobic surface, regardless of solution pH. The oil-wet solids display a charge of 5 x 10-7 equivalents/m^2, roughly half the charge of the water-wet solids, and are positively charged below pH 5 and negatively charged above pH 5.

One of the central issues in our research is to understand how and why NMR measurements are affected by the wettability of the solid surface. The measured NMR parameter for a porous, fluid-saturated sand sample is the T1 proton relaxation time, which can be related to the material properties of the sample by the equation:

$$\frac{1}{T_1} = \rho \frac{S}{V} + \frac{1}{T_{1b}}, \qquad (1)$$

(1) where r is the surface relaxivity, S/V is the surface area to volume ratio of the pore space and T1b is the relaxation time for the bulk pore fluid. The NMR parameter that is expected to be closely related to the state of the solid surface is r, which can be considered to be a measure of the ability of the surface to shorten the relaxation time. Previous work has suggested that r should be highest in water-wet systems and should decrease in oil-wet or hydrophobic systems. These studies however neglected to account for the role of the chemistry of the solid and fluid.

In our experiments with water-wet pure quartz sand and water-wet silica gel, we have found that r is close to zero (approximately 10^{-4} mm/s) and is constant over all pH values. For the pure quartz sand, with its very low surface area to volume ratio (S/V), we found that the measured relaxation time T1 (2.9 s) is the same as the bulk fluid relaxation time T1b within experimental error. For silica gel, with a much larger S/V, T1 decreased to 1.6 s. This set of experiments has conclusively shown that the larger values of r commonly reported for natural sands cannot be explained by the presence of water-wet solid surfaces alone.

The factor that must be accounted for in order to interpret and use NMR measurements on natural sands is the effect of paramagnetic species, which can be present in the pore fluid, as separate mineral grains, as ions adsorbed to sand surface sites or as a thin layer of solid precipitated onto the sand grains. The relaxation time of bulk fluids containing Fe^{3+} was found to decrease exponentially with increasing concentration. This illustrates the importance of accounting for the chemistry of the pore fluid in interpreting NMR measurements of fluid-saturated materials. When insoluble iron(III) titanium oxide grains were mixed with silica gel at pH 5.7, T1 decreased exponentially from 1.6 to 0.6 s with increasing fraction of paramagnetic mineral (0 to15% by weight). This decrease in T1 was caused by a dramatic increase in r due to the presence of paramagnetic solid surfaces, with no change in the wettability of the surface. In order to study the effect of adsorbed paramagnetics, pure quartz sand was equilibrated with 0.5 ppm Fe^{3+} solution at pH 1 and at pH 3. At pH 1 no iron was adsorbed to the surface and T1 remained the same as T1b; but at pH 3, 5-20% of the iron was adsorbed and T1 decreased 0.7 s due to an increase in r. We can conclude that a paramagnetic ion adsorbed to the sand surface has a much greater effect on relaxation than a dissolved paramagnetic ion. This experiment also shows that the surface charge of the solid surface affects NMR indirectly by affecting the adsorption of paramagnetic ions.

Having documented the effect of paramagnetics, we can develop a better understanding of the effect of oil-wet surfaces on NMR measurements. Here again we find that paramagnetic species play an important role in relaxation processes, both through changes in the pore fluid chemistry and through the addition of paramagnetic species to the solid surface. A series of experiments with oil-wet materials is in progress at this time.

Dielectric measurements are, in general, less sensitive than NMR to molecular-scale interactions at the solid/fluid interface. As a result, our approach has been to first complete the NMR component of our study, in order to develop a clear understanding of the physics and chemistry of the various solid/fluid systems. In the first set of dielectric experiments, conducted with water-wet, hydrophobic and oil-wet quartz sands, we found that the change in the electrical conductivity of the pore fluid, due to chemical equilibration with the three types of surfaces, was the dominant factor in the dielectric measurements. As a result, the dielectric constant of the oil-wet sand was much greater than that of the water-wet sand. In repeat experiments, the pore fluid chemistry has been set to eliminate this effect. We find that the presence of an oil-wet or hydrophobic surface causes a decrease in the dielectric constant at frequencies greater than 100 kHz, but an increase at lower frequencies. We are presently investigating the role of surface conduction associated with the properties of the oil-water interface in oil-wet sands.

Planned Activities

In months 20 to 26 of this project we plan to complete the NMR experiments with the oil-wet and hydrophobic sands. In months 22 to 26 we will conduct NMR experiments as a function of temperature, to assess the use of NMR as means of monitoring the adsorption and desorption of organics. In month 26 we will select NMR experiments that will be repeated using a lower field spectrometer, and these will be conducted in months 26 to 30. The dielectric experiments, which will parallel the

NMR experiments, will continue through month 32. The last four months of the project will be spent on analysis, interpretation, and modeling of data and preparation of final papers/reports, with some time spent as needed to repeat specific measurements.

High Frequency Electromagnetic Impedance Measurements for Characterization, Monitoring and Verification Efforts

Ki Ha Lee, Lawrence Berkeley National Laboratory

Alex Becker, University of California
Louise Pellerin, Lawrence Berkeley National Laboratory

Research Objective

Non-invasive, high-resolution imaging of the shallow subsurface is needed for delineation of buried waste, detection of unexploded ordinance, verification and monitoring of containment structures, and other environmental applications. Electromagnetic measurements at frequencies between 1 and 100 MHz are important for such applications, because the induction number of many targets is small due, and the ability to determine the dielectric permittivity in addition to electrical conductivity of the subsurface is possible. Earlier workers were successful in developing systems for detecting anomalous areas, but no quantifiable information was accurately determined. For high resolution imaging, accurate measurements are necessary so the field data can be mapped into the space of the subsurface parameters. We are developing a non-invasive method for accurately imaging the electrical conductivity and dielectric permittivity of the shallow subsurface using the plane wave impedance approach, known as the magnetotelluric (MT) method at low frequencies. Electric and magnetic sensors are being tested in a known area against theoretical predictions, thereby insuring that the data collected with the high-frequency impedance (HFI) system will support high-resolution, multi-dimensional imaging techniques.

Research Progress and Implications

The summary of the work to date is divided into three sections: equipment procurement, instrumentation, and theoretical developments. For most earth materials, the frequency range from 1 to 100 MHz encompasses a very difficult transition zone between the wave propagation of displacement currents and the diffusive behavior of conduction currents. Test equipment, such as signal generators and amplifiers, does not cover the entire range except at great expense. Hence we have divided the range of investigation into three sub-ranges: 1-10 MHz, 10-30 MHz, and 30-100 MHz. Results to date are in the lowest frequency range of 1-10 MHz. Even though conduction currents dominate in this range, as in traditional electromagnetic exploration methods, little work has been done by the geophysical community above 500 kHz.

Equipment Procurement: Test equipment for our frequency sub-ranges can be very expensive and specialized, hence we are borrowing equipment whenever possible. The magnetic field sensors and a vector signal analyzer, providing 2 channels of data acquisition in addition to a reference signal, purchased as a part of the VETEM project, were borrowed from the DOE Grand Junction

Project Office. We are borrowing power amplifiers from Lawrence Livermore National Lab. As a part of the EMSP funding we have acquired two lock-in amplifiers and a PC computer with GPIB software, for data acquisition. We currently have the capability to generate a transmitter signal and amplify and measure two output signals in the 1-10 MHz range.

Instrumentation: The magnetic field sensors, two EMCO Model 6507 loop antennae designed to function accurately to 30 MHz, were tested in the 1-10 MHz range, and we concluded that measurements to 10 MHz (and probably 30 MHz) can be made reliably with commercially available sensors.

Three electrical field sensors - a toroid, stub, and capacitively coupled antennae were tested. A small toroid was fabricated, but because of the size and relatively low frequency (1-10 MHz) a strong signal was needed to excite the sensor. Initial tests in a 60-100 volts/m source field correspond roughly with predicted responses. A larger toroid, with greater sensitivity, will be used for future testing. A modification to the initial design canceled the emf caused by an axial magnetic field component. Electronics needed for minimal amplification are being added to the toroid and the cable length is being shortened to minimized secondary responses.

Two ARA stub dipole antennae, designed to be used outside the influence of the earth, were acquired. Preliminary results of measured responses did not agree with the predicted response. After taking into account the radiation pattern of an imperfect conductor (the earth) and the reciprocity principle, we have been able to match the theoretical and the field response. A prototype capacitive antennae was deployed and when teamed with the EMCO magnetic field measurements, results match well with that determined from other data.

Theoretical Developments: The one-dimensional numerical investigating of approaches to compensate for the non-vertical propagation of the fields and effective parameterization of the data is complete. Measurements of the electric field at two locations simultaneously are necessary to estimate the horizontal component of the wavenumber due to non-vertical propagation. Traditional parameterization of MT data, expressed as apparent resistivity and phase, did not appear to be suitable at high frequency due to multiple reflections in any resistive layers. Data inversion seems to be a more accurate method with which to present the data.

Planned Activities

Work will continue on the analysis of the antennae through higher frequencies, and the development of the three-dimensional (3D) HFI analysis package through the rest of the FY98. A finite difference code, a finite element code and a high frequency thin sheet solution are being tested for use in the 3D analysis. The specifications for the HFI system are being written as the sensors are being tested.

Advanced High Resolution Seismic Imaging, Material Properties Estimation and Full Wavefield Inversion for the Shallow Subsurface

Alan Levander, Rice University

Colin A. Zelt, Rice University
William W. Symes, Rice University

Research Objective

We are developing advanced seismic data processing, imaging, and inversion methods for high resolution seismic reflection/refraction imaging and material property estimation of the shallow subsurface. The imaging methods are being developed to map the structural and material properties of aquifers and aquitards.

Research Progress and Implications

This report summarizes work completed in the first seven months of a three year project which began in November 1997. Our research is proceeding along three lines : data acquisition, data processing, and algorithm development.

Last fall we visited a waste site at Hill Air Force Base near Ogden, Utah as a potential site for a high resolution seismic study. Unfortunately the onset of winter precluded field operations last fall. The region has been studied extensively with drilling, electromagnetic studies, as well as some previous seismic refraction investigations. The seismic target is a paleostream channel in the top of a clay layer along which trichloroethylene (TCE) solvents collect in low spots. There are a number of obstacles to overcome to use this as one of our test sites, but these are fairly common problems encountered in shallow imaging. The previous refraction studies appear to show that the near surface seismic velocity is very low (there is some ambiguity in the reports, but it looks like 300-400 m/s is the near surface velocity), and the target we are interested in is very shallow (15m), requiring a rather high frequency seismic source (200-400 Hz). On the other hand the near surface is rather poorly consolidated sands and gravels which implies high seismic attenuation. We are examining various seismic sources which might be utilized. In the meantime, we have a rather lengthy work plan to prepare to gain access to the site, and we have an OSHA safety training course to take. We also visited a DOE site at Lawrence Livermore National Lab which has also been extensively studied previously. In this case the site has been investigated with crosswell and surface seismics, which showed a very high near surface seismic attenuation. It appears to us that this may also pose some interesting challenges that would be worth investigating.

In the meantime, we are processing high resolution data we acquired prior to the beginning of this study. In 1996 we conducted a high resolution seismic survey along the rim of an open pit porphyry copper mine in Southwest New Mexico. The survey employed reflection, refraction and transmission profiles in order to image features exposed in the mine walls. The local geology consists of a sedimentary layer, the Gila conglomerate, overlying crystalline rock. The crystalline rock includes unaltered country rock and mineralogically altered rock that is the ore for the local mining operation. For this study, targets for imaging include bedding within the Gila conglomerate; the unconformity between the sedimentary layer and the crystalline basement; the contact between altered and unaltered crystalline rock; and near surface structural features.

Dynamite and hammer data were acquired, processed separately, and then combined into a total mine depth section. The combination of data from the two source types provides seismic resolution at two slightly different scales (bandwidth of 20-80 Hz for dynamite and 60-150 Hz for hammer) and

a validation of individual source results. Following initial data clean up, bandpass filters were used to remove low frequency and 60 Hz noise. Various types of deconvolution including surface consistent decon were applied to the data. Surface-consistent decon produced the best results. Data from both source types were still dominated by strong ground roll and linear noise masking the weaker reflections. The coherent noise was removed with f-k filters.

An initial velocity model was constructed using ray-based 2 D inversion of the surface to surface travel times. The model included the strongly variable velocity in the most shallow subsurface, but was unable to resolve velocity variations below the sedimentary layer. Extending the model to 2.5 D by incorporating travel times from transmission and refraction data, allowed us to adequately constrain velocities below the sedimentary layer, and construct a velocity model for depth migration. Following CMP processing, data from both source types were poststack depth migrated using the velocity model and combined into a seismic section of the total depth of the mine.

The seismic results correlate with visible expressions of the formations within the walls of the mine. Specifically, we see: 1) Sedimentary bedding within the conglomerate, 2) The contact between sedimentary sequence and gneiss, 3) The contact between mineralized and unaltered gneiss, and features such as 4) The fracture zone at the contact between mineralized and unaltered gneiss, which acts as a conduit for groundwater movement.

The feasibility of simultaneously imaging differences in lithology, contrasts due to mineralogic alteration, as well as structural faulting has implications for directing the mining operation. Locating structural features, such as those controlling groundwater flow, also has environmental applications. The consistency of the independently processed data sets provided a valuable internal check for the validity of the overall processing scheme.

In terms of algorithm development we have continued work on wide-angle migration and travel time tomography. In order to determine the three-dimensional long-wavelength velocity model needed for pre-stack depth migration, a traveltime tomographic approach is being developed for both refracted and reflected arrivals. The forward step uses a finite difference solution of the eikonal equation, and therefore is ray-theory accurate. Traveltimes from pre and post critical arrivals are used in a combined, simultaneous reflection and refraction tomographic method, much like that developed by Zelt and Smith (1992) for two dimensions, except on a uniform grid. Tomographic inversion for refracted arrivals has already been developed and thoroughly tested (Zelt and Barton, 1998), and the forward calculation of reflection traveltimes from an arbitrary surface defined on a uniform grid has also been completed. Current work centers around including the reflected arrivals in a regularized inverse scheme, and “tying” the velocities between the layers to the interfaces.

Planned Activities

The 3-D travel-time tomography should be completed by the end of the first year of the proposal. Within the next 6 months we will conduct at least one high resolution seismic survey and possibly two, one of which will be either the Hill AFB site or LLNL, the other of which will be a control site at Rice. We already have traditional CMP data from this site. We will refine the migration velocity focusing algorithms we have developed, and apply them to the test near vertical to wide-angle seismic datasets that we collect.

Seismic Surface-Wave Tomography of Waste Sites

Timothy L. Long, Georgia Institute of Technology

Research Objective

The objective of the Seismic Surface Wave Tomography of Waste Sites is to develop a robust technique for field acquisition and analysis of surface wave data for the interpretation of shallow structures, such as those associated with the burial of wastes. The analysis technique is to be developed and tested on an existing set of seismic data covering the K-901 burial site at the East Tennessee Technology Park. Also, a portable prototype for a field acquisition system will be designed and developed to obtain additional data for analysis and testing of the technique. The portable analysis system will display an image representing the shear-wave velocity structure. The image would be developed in the field from successive data samples.

Research Progress and Implications

As of May 1998, we established compatibility with computer programs at Georgia Tech and computed a preliminary singular value decomposition solution for the K-901 data. The analysis included modeling of surface wave dispersion and analysis of velocity structure. The analysis demonstrated that we needed additional field data to verify the conclusions and provide independent confirmation of velocity structure. The K-901 site data were obtained with 8 Hz geophones. The frequencies below 8 Hz are strongly attenuated in such recording instruments and are difficult to analyze. In particular, group velocities can have multiple answers for a given frequency. Consequently, without a record of the low-frequency energy, we found it difficult to identify the portion of the dispersion curve responsible for the seismogram. In particular, it was difficult to determine if the reverse dispersion observed in the frequencies above 8 Hz was caused by a low velocity layer or caused by observing only the frequencies above the group velocity minimum. In either model, synthetic seismograms can be made to match the observed data for the higher frequencies. The contract for the proposed work was completed in December. The field work was completed in March. The pending final report from William Doll at the Oak Ridge National Laboratory will provide background information on the test site and new uphole and seismic refraction data and interpretation for use in confirming the tomographic inversion.

The acquisition system and software were designed during the first year. The final system will consist of four programs: Data Acquisition, Trace Display/Correction, Velocity Analysis and Tomographic Inversion. During the second year the Data Acquisition and Trace Display/Correction programs were converted to run as compiled visual basic programs under windows NT. The original programs were in quick basic and ran under DOS 6.2. Windows NT allows simultaneous data acquisition not possible under DOS operating systems. The basis for the Velocity Analysis program is under development. The difficulty in determining group velocity is a major challenge in the inversion for near-surface velocity structure. Our original analysis used time-frequency analysis techniques to determine the arrival time of specific frequencies of energy in the surface wave. In particular, we used maximum entropy spectral estimators to optimize the resolution of frequency in small time increments. However, the uncertainty in the arrival time of a particular frequency was complicated by multiple modes and instrument response that introduced errors which were too large to allow a robust inversion. For the Tomographic Inversion program, we have experimented with the algebraic reconstruction technique (ART) with applications to synthetic data. The programs are currently running efficiently on a 486 vintage machine which has been successful in field acquisition trials. Program documentation is available for the first two from tim.long@eas.gatech.edu.

Using the acquisition system, we have obtained data from four sites with differing surface velocity characteristics. The first is the Cobb County test facility, a site for which we have knowledge of the

location of various buried objects. The second and third are the sites of two earthquake monitors, stations GLS and HSP, where the near-surface velocity structure could assist other studies. The fourth is the ORNL K-205 site. At the ORNL K-205 site we recorded with 1.0 Hz geophones to obtain dispersion relations at frequencies below 8 Hz. We also obtained refraction data and data for tomographic inversions in two smaller sections of the K-205 test site.

Planned Activities

The third year, June 1, 1998-September 30, 1999, will be used to refine the techniques for surface wave inversion for the tomographic geometry. Principally we will implement the Velocity Analysis and Tomographic Inversion programs. During the coming summer quarter, we will be investigating interpretation techniques that will reduce scatter in group velocity estimates. In particular, we will be examining the use of the relation between perturbations in phase and group velocity to constrain group velocity measurements. The principal advantage is that the phases are highly and accurately correlated between adjacent traces. For the Tomographic Inversion program we will program the algebraic reconstruction technique to process data from the Velocity Analysis program.

We will continue to test the analysis on data obtained from the Cobb County test facility, seismic station HSP, seismic station GLS and the K-901 site. Other sites will be tested as appropriate and as made available when sufficient auxiliary data are available to make the study useful.

For 1999 we will consider transfer of the system to a faster portable computer. The existing system is sufficient for data acquisition and correction. However, it is a desktop version (hence inconvenient in the field) and not fast enough to use for simultaneous acquisition and inversion. We have delayed this because of obvious price and performance considerations.

Collaborative Research: Hydrogeological-Geophysical Methods for Subsurface Site Characterization

Gary Mavko, Stanford University

Yoram N. Rubin, University of California at Berkeley

Research Objective

The general purpose is the subsurface characterization of LLNL superfund site. The goal is to get the most accurate map of the hydrogeological parameters, necessary for modeling and designing the cleanup efforts at the site, using well log data and remote sensing geophysical techniques.

Research Progress and Implications

In the second year of the project progress has been made in several areas: gathering and interpreting Vertical Seismic Profile (VSP) and Electromagnetic (EM) surveys; investigating the impact of various seismic measurements on upscaling of rock physics relations between sediment properties; and developing a new approach to integrate geophysical and hydrological data using state of the art methods to characterize the subsurface lithology.

Vertical Seismic Profile data has been gathered from selected wells at the Treatment Facility D (TFD) during April 1996 and April 1998. The most striking finding here is the detection of anomalies

related to saturation conditions. Preliminary results have revealed three anomalously low acoustic velocity zones with velocities below 1000 m/s; this is lower than the natural acoustic velocity in saturated media by pure water (1500 m/s).

These three zones appear to be associated with HSUs 3a, 3b and 5. Velocities below 600 m/s have been revealed in the 3a and 3b HSUs (**http://www.ce.Berkeley.edu/~ezzedine/DOE/paul.html**). We believe that these anomalies are indicative of partial saturation. This explanation is supported by the water samples taken from pumping stations near the VSP well sites which appears to contain air bubbles. A gas analysis of water samples has not yet been performed. We hypothesize that this gas can be either air being sucked-in from the vadose zone above the water table, or from some chemical reaction. As a matter of fact, the natural water table level at this site was around 20m below ground surface before any large scale pumping began, and had dropped to 25.5m, in April 98. Furthermore, some of these low velocity zones are occurring not only in the major free-flowing sand or gravel parts of the HSU, but in boundary layers of silty sand either above or below the main HSU conductor.

An electromagnetic survey was conducted at the site during June 4-25, 1997, and we worked on its interpretation. Seven cross well EM data sets were collected. Both 1D and 2D simulations, approximating the actual site and survey setup, were conducted. The 1D simulations were conducted using the code EM1D for one data set. Newman and Alumbaugh's 3D forward code was used to simulate the response of both a resistive layer (representing HSU 4) and a conductive layer at the same location. Three separate inversion algorithms were applied to the data: Newman and Alumbaugh's 2.5D finite difference and integral solution algorithm, Alumbaugh's iterative Born approximation with a cylindrical symmetry, and Tseng's 3D extended born approximation. The field EM data are still being analyzed.

A synthetic model consistent with the shallow unconsolidated nature of the sediments at the site was built, to investigate the impact of various seismic measurements on upscaling petrophysical relations such as velocity-porosity and velocity-clay relations. The available well logs were used to assign distributions of physical properties to different facies. Care was taken to build the model self-consistently by taking into account relations between facies type, clay content, porosity, resistivity, and velocity in unconsolidated media. Once a consistent earth model was built, we simulated a surface seismic image using a single scattering, frequency domain, and the Born filter approximation methods, which allowed us to estimate the impact of various measurement geometries and bandwidths on the spatial distribution of the imaged seismic velocity. Cross section of the 'true' fine scale velocity model, and the synthetic surface seismic image reveal a smoothing effect caused by the limited frequency bandwidth and aperture of the simulated seismic measurement (**http://water.stanford.edu/doe/**).

Velocity-porosity and velocity-clay relations which may be perfectly correlated at a fine scale appear to have large scatter when imaged at a coarser scale. We used the Born filter approximation as well as traveltime algebraic reconstruction tomography to explore the scatter introduced by the imaging in the bilinear velocity-clay relation for a dispersed binary mixture model of shaly sand sediments. We built a simple filter in the frequency domain to estimate the seismic response of various measurement scenarios. The filter response was designed to match a tomographic image obtained by numerically simulating wave propagation for a cross-well geometry, picking the synthetic seismograms, and inverting the traveltime pick using an ART algorithm. The frequency domain filter provides a very fast and efficient way to explore multiple stochastic realizations and scenarios such as varying saturations, pressures, and clay content, without having to do a full finite-difference wave propagation and inversion. This tool can be used to map out the space of uncertainty by applying it to large numbers of stochastic simulations of the random velocity field.

One of the important issues in using rock physics to interpret seismic and VSP velocities at the site is to understand the variations of velocity with lithology and clay content relative to the velocity sensitivity to pore fluid saturations. Therefore, we compared the VSP velocities for different lithologies to laboratory data on loose sediments. The VSP velocities are comparable to the laboratory data, suggesting that laboratory derived velocity models may be applicable at this site. The velocities do not show a strong dependence on lithotype.

A conceptual data-driven approach for hydrogeological mapping based on the well logs, and cross well geophysical data has been developed (**http://www.ce.Berkeley.edu/~ezzedine/DOE/**).

The general framework is hierarchical stochastic, and it consists of three major steps, starting from mapping lithofacies, and ending in high resolution hydrogeological mapping: (1) the unknown image of the sand/silt cross-section is developed as a particular realization of a two or three-dimensional, statistically homogeneous binary random field. Sequential Indicator Simulation for lithology estimation is employed for that purpose. The indicator is defined by its unconditional univariate probability distribution function (pdf), or can be made conditional to binary-valued observations of lithology at the wells, and can be further updated if geophysical data is available and is informative. The outcome of this step is a complete stochastic characterization of the spatial distribution of sand and silt, and a series of lithology images; (2) each of the lithology images generated are overlain with an image of the shaliness generated using facies-specific pdf. The spatial correlation structure of the shaliness is determined by its variograms facies specific. The outcome of this step is a serious of shaliness images, which will be converted to resistivity images. Our focus on shaliness stems from the observation that it displays a well defined spatial correlation structure, it correlates well with resistivity, and can be used to infer other hydrogeological properties; (3) a prior non stationary pdf is assigned to each point over a regular grid. These pdfs are obtained from the petrophysical relationship, once a location is identified as being as either in the sand or silt facies and a measurement or generated value of the shaliness is specified. Unless additional information becomes available, prior resistivity pdf's can be used for generating resistivity values. To further update the pdf's of the resistivity, we adopted a Bayesian framework where the prior resistivity pdf's are combined with the pdfs of the likelihood resistivity image obtained from Electromagnetic (EM) surveying to get an updated resistivity image.

These concepts were implemented to one HSU using all available well data at TFD at LLNL superfund site. Extension to all HSUs is straightforward. Statistical analysis of the updating procedure showed the tremendous improvement in the estimation of the posterior resistivity image.

Planned Activities

Several activities are planned in all areas for the third year of the project:

(1) more VSP data acquisition has to be done to get an adequate areal coverage of low velocity zones to map them. Also, an adequate hydrostratigraphic and/or chemical model will have to be worked out to explain these low velocity zones. If this model directly links pumping activity with the areal spread of these low velocity zones, then perhaps continuous (time lapse) VSP surveys may be performed to help control and direct which wells to pump from, and at what rates;
(2) EM cross well surveys will be analyzed and compared with the VSP surveys;
(3) results of VSP and EM will be integrated in the Bayesian stochastic hydrogeological-geophysical subsurface characterization model; and
(4) the integration between EM and VSP will be further investigated using synthetic studies.

3-D Spectral IP Imaging: Non-Invasive Characterization of Contaminant Plumes

F. Dale Morgan, Massachusetts Institute of Technology

William Rodi, Massachusetts Institute of Technology
David Lesmes, Boston College

Research Objective

The overall objective of this project is to develop the scientific basis for characterizing contaminant plumes in the earth's subsurface using field measurements of induced polarization (IP) effects. Three specific objectives towards this end are:

1. Understanding IP at the laboratory level through measurements of complex resistivity as a function of frequency in rock and soil samples with varying pore geometries, pore fluid conductivities and saturations, and contaminant chemistries and concentrations.
2. Developing effective data acquisition techniques for measuring the critical IP responses (time domain or frequency domain) in the field.
3. Developing modeling and inversion algorithms that permit the interpretation of field IP data in terms of subsurface geology and contaminant plume properties.

Research Progress and Implications

Laboratory Studies

Our laboratory experiments to date are described in Appendices A and B, which consist of two papers submitted to the annual SAGEEP conference (Frye et al., 1998; Sturrock et al., 1998). Our experiments involved measurements of complex resistivity vs. frequency on a suite of brine saturated sandstone samples. In one set of experiments, the fluid chemistry (pH, ionic strength, and cation type) was varied. In a second set of experiments, the microgeometry of the rock matrix was varied. The experiments showed that spectral IP responses are sensitive to subtle variations in both the solution chemistry and rock microgeometry. The results demonstrate that spectral IP responses have the potential of being sensitive indicators of in-situ chemistry and microgeometry, the latter of which may be related to the hydraulic properties.

Data Acquisition

We have been looking in some detail at the effects of electromagnetic coupling and how to practically deal with it. In this area, our results to date are summarized in Vandiver (1998).

Modeling and Inversion

Our progress in the development of modeling and inversion algorithms for IP is described in Appendix C, a paper submitted to the annual SAGEEP conference (Shi et al., 1998). We have developed algorithms for forward modeling and inversion of spectral IP data in 3-D media. The algorithms accommodate a general earth model with a complex electrical conductivity as a function of frequency and 3-D spatial position. Using regularization and optimization techniques, the inversion algorithm obtains a 3-D image of resistivity amplitude and phase for each frequency contained in the data set. We have begun testing our algorithms on synthetic data generated from a simple model of a contaminant plume. The complex resistivity parameters of the background medium and plume are based on the laboratory results described above.

Planned Activities

In addition to continuing studies in the above mentioned 3 areas, we will be conducting a detailed 2D IP survey at the Aberjona, Superfund Site in Woburn, MA.

Other Access To Information

Results of this research project were presented at The Symposium on the Application of Geophysics to Environmental and Engineering Problems, held March 1998 in Chicago and sponsored by the Environmental and Engineering Geophysical Society. The following three papers were presented and are published in the conference proceedings:

Frye, K.M., D.P. Lesmes, and F.D. Morgan, The influence of pore fluid chemistry on the induced polarization response of rocks and soils, SAGEEP Proceedings. pp. 771-781.

Shi, W., W.L. Rodi, and F.D. Morgan, 3-D induced polarization inversion using complex electrical resistivities, SAGEEP Proceedings. pp. 785-795.

Sturrock, J.T., D.P. Lesmes, and F.D. Morgan, The influence of micro-geometry on the hydraulic permeability and the induced polarization response of sandstones, SAGEEP Proceedings. pp. 859-869.

Vandiver, Amy, 1998, Analysis of the Effects of Inductive Coupling in Induced Polarization Surveys of Environmental Contaminants, MIT BS Thesis.

Seismic-Reflection and Ground Penetrating Radar for Environmental Site Characterization

Don W. Steeples, University of Kansas

Richard Plumb, University of Kansas

Research Objective

The project's goals are threefold:

1. To examine the complementary site-characterization capabilities of modern, three-component shallow-seismic techniques and ground-penetrating radar (GPR) methods at depths ranging from 2 to 8 m at an existing test site;
2. To demonstrate the usefulness of the two methods when used in concert to characterize, in three-dimensions, the cone of depression of a pumping well, which will serve as a proxy site for fluid-flow at an actual, polluted site; and
3. To use the site as an outdoor mesoscale laboratory to validate existing three-dimensional ground-penetrating radar and seismic-reflection computer models developed at the University of Kansas.

To do this, useful seismic and GPR data are being collected along the same line(s) and within the same depth range. The principal investigators selected a site in central Kansas as a primary location and, although the site itself is not environmentally sensitive, the location chosen offers particularly useful attributes for this research and will serve as a proxy site for areas that are contaminated. As part of an effort to evaluate the strengths of each method, we will repeat the seismic and GPR surveys on a seasonal basis to establish how the complementary information obtained varies over time. Because

the water table fluctuates at this site on a seasonal basis, variations in the two types of data over time also can be observed. Such noninvasive in-situ methods of identifying and characterizing the hydrologic flow regimes at contaminated sites support the prospect of developing effective, cost-conscious cleanup strategies in the near future.

Research Progress and Implications

As of the end of May 1998, the project is on schedule. The first field work was conducted using both of the geophysical survey methods in October of 1997, and the second field survey employed both methods in March of 1998. One of our stated tasks is to reoccupy the same survey line on a quarterly basis for two years to examine change in both the seismic reflection data and the ground-penetrating radar (GPR) data over time. Two factors drive these changes: First, the soil-moisture conditions vary on a seasonal basis at the site. Second, the water table rises and falls on the order of one meter in response to changes in the level of the Arkansas River and in response to the many irrigation wells found nearby. At our test site in the Arkansas River alluvial valley near Great Bend, Kansas, surface material consists of unconsolidated medium- to coarse-grained sand interspersed with clay stringers and lenses deposited by the Arkansas River. A hand-augered test hole 5 meters from the seismic line revealed sand to a depth of about 1.5 meters, where a hard pan was found—presumably a clay layer. At the time of our seismic and GPR surveys, the water table was at a depth of 2.1 meters, based on a measurement in a test well located 25 meters from the seismic line. A well drilled about 40 meters away from the seismic line encountered bedrock (a fine- to medium-grained Cretaceous-age sandstone) at a depth of 29 meters.

Our experiments with GPR included antennas with 110, 225, and 450 MHz center frequencies. Both common-offset and common-midpoint (CMP) surveys have been conducted. The CMP surveys greatly improved signal-to-noise ratio but did not greatly increase the depth from which we were able to acquire interpretable data. Using GPR, we were able to see the water table clearly at a depth of about two meters and found indications of stratigraphic variation along the line.

In the past, shallow seismic-reflection methods have been used to image the subsurface from 2 to 30 meters. Because of near-source nonelastic deformation and insufficient receiver density, these technologies have not been adequate for imaging ultra-shallow subsurface geology. Modifying the field layout of the geophones and using an alternate seismic source have allowed us to image the subsurface from 0.6 to 2.1 meters using seismic reflections. In our experiments, three distinct reflections were observed within this range while using surface sources and receivers at our test site in the Arkansas River valley and were confirmed by 4th-order, finite-difference wave-equation modeling.

Our progress so far toward achieving workable ultra-shallow seismic reflection imaging is largely attributable to an improved ability to measure the near-source wavefield. To accomplish this, we collected data using a single 100-Hz geophone group interval of 5 cm. In contrast, typical “shallow” seismic surveys have receiver-group intervals of 1 m or more. Because we increased receiver coverage by a factor of 20 or more, our ability to delineate and improve the coherence of ultra-shallow reflections over other interfering phases was enhanced. Seismic-source energy was provided by a single shot from a .22-caliber rifle using subsonic solid-point short ammunition. We found that other larger, more powerful shallow seismic exploration sources tested at the site (commercial seisguns and sledgehammers) generated enough near-field nonlinear deformation to render near-source (i.e., ultra-shallow) reflection information undetectable.

Preprints of reports based on this work have been submitted to Science, Geophysics, and the expanded abstracts volume for the 1998 Society of Exploration Geophysicists (SEG) meeting in New Orleans in September as well as to the AAPG Explorer (see Other Access To Information section for a listing of titles and authors).

Planned Activities

The third set of field surveys will be conducted in June 1998, and data will be processed and interpreted as originally proposed.

Other Access To Information

Baker, Gregory S., Chris Schmeissner, Don W. Steeples, and Richard G. Plumb (1998) Seismic reflections from depths of less than two meters: submitted to Science, May 1998.

Steeples, D. W., G. S. Baker, C. Schmeissner, and B. K. Macy (1998), Geophones on a board: submitted to Geophysics, in review.

Steeples, D. W., and Gregory S. Baker (1998), Near-surface contributions to seismic static corrections: AAPG Explorer, in press.

Baker, G. S., R. G. Plumb, D. W. Steeples, M. Pavlovic, and C. Schmeissner (1998), Coincident GPR and ultrashallow seismic imaging in the Arkansas River Valley, Great Bend, Kansas: SEG Expanded Abstracts, SEG 1998 International Meeting, New Orleans, in press.

Baker, G. S., D. W. Steeples, C. Schmeissner, and B. K. Macy, (1998), In-situ, high-resolution P-wave velocity measurements within 1 m of the Earth's surface: SEG Exp. Abstr., in press.

Steeples, D. W., G. S. Baker, C. Schmeissner, and B. K. Macy (1998), Geophones on a board: SEG Exp. Abstr., in press.

Enhancements to and Characterization of the Very Early Time Electromagnetic (VETEM) Prototype Instrument and Applications to Shallow Subsurface Imaging at Sites in the DOE Complex

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Weng C. Chew, University of Illinois at Urbana-Champaign

Research Objective

The objective of this project is to enhance the state-of-the-art of electromagnetic imaging of the shallow (0 to 5 m) subsurface in electrically conductive media where ground penetrating radar (GPR) provides insufficient penetration and time domain electromagnetic (TEM) systems provide insufficient resolution. This objective is being pursued by instrumentation enhancements to the existing very early time electromagnetic (VETEM) system coupled with physical and numerical modeling. Success in this endeavor will improve the speed and accuracy of waste pit and trench location and characterization, and could have additional applications to shallow DNAPL and LNAPL spill and cleanup monitoring, clay cap integrity assessment, and landfill stabilization monitoring. This could result in significant savings in time and money during characterization, remediation, and decommissioning of facilities.

Research Progress and Implications

This report summarizes accomplishments after 8 months of a three-year project. We have focused mainly on instrumentation and numerical modeling during this time.

Examination of data recorded with the VETEM system, as it existed in 1995, showed very encouraging response to relatively shallow buried conducting targets, but also showed a need for improved response to shallow dielectric (non-conducting) objects and also for greater depth of investigation for conducting objects. The need for numerical and physical modeling to optimize system design and to enable better interpretation of data was also clear.

To address the need for better response to shallow buried dielectric objects, we have designed,

built, and laboratory tested a new transmitter that puts out several times more current (> 5 A as compared to ~ 1 A for the existing transmitter) with a much shorter risetime (~ 3 ns as compared to ~20 ns fall time for the existing transmitter). This transmitter is ready for field tests, but we anticipate that we may require new antennas (both magnetic loop and electric dipole) to achieve the best results from this transmitter.

The need for deeper penetration was addressed by the design and construction of another transmitter that can drive up to 30 A into a new larger loop antenna. The current rises almost linearly at a rate of about 6 A per microsecond and has a fall time of about 120 ns. The 30 A transmitter has been mated to a new magnetic loop antenna with 10 times the area of the original antennas. A similar larger receiving antenna has been constructed. This new transmitter/antenna combination is ready for field tests.

We now have three distinctly different transmitters and two sets of loop antennas with a factor of 10 difference in area between the two sets. Both sets are single-turn to minimize inductance.

Another factor in depth of penetration is the separation between the transmitting and receiving antennas. The original antenna cart limited this separation to a 2 m maximum. We have designed and built a new cart that will permit separations of more than 4 m. In addition, the new cart is stiffer than the old one to reduce any potential of errors caused by changes in relative antenna alignment. Construction of non-metallic materials has been retained. The new cart will be ready for the July, 1998 field tests.

In order to transport the new antenna cart, a trailer large enough to carry it is necessary. This trailer has been obtained and is currently being equipped to transport VETEM and other geophysical equipment, and for use as a mobile remote site in-the-field data processing facility. It will be ready for the July, 1998 field tests.

To improve signal-to-noise performance and to allow better potential for technology transfer, a commercial digitizer/signal averager has been selected and ordered. It is not clear whether delivery will be in time for anticipated field tests in July, 1998. This unit will replace one built by the USGS that uses high speed memory chips that are no longer readily available. The USGS system remains as a back-up.

In order to take full advantage of the new transmitters and antennas, a new receiver will be required with progammable bandwidth, and greater dynamic range. A laboratory prototype has been built and is being evaluated, but a field worthy version will not be available in time for the July, 1998 field tests. We will use the existing receiver.

An outdoor buried object geophysical test range suitable for VETEM, GPR, and EM system calibration and physical modeling is planned for the Denver Federal Center. A proposal has been submitted to the General Services Administration for approval.

Numerical modeling of the effects of buried dielectric and conducting objects has been done using a scattering formulation and method of moments solution requiring the evaluation of large numbers of Sommerfeld integrals. In order to make such an approach practical at high frequencies, fast evaluation of Sommerfeld integrals is essential. The very fast leading-order approximation method has been generalized in this work to allow lossy (conductive) as well as lossless cases. The results were applied to calculate primary, reflected, and scattered fields from a buried dielectric cuboid and a conducting plate.

The results of the numerical modeling show that the scattered field from the conducting plate is greater in amplitude and distinctively different in shape than the scattered field from the dielectric cuboid. The numerical modeling also demonstrated the orders of magnitude difference in amplitude between primary and scattered fields. This is also observed in field data and demonstrates the need for a receiver with extremely wide dynamic range, as we had anticipated

Planned Activities

The next major activity will be field tests at the Idaho National Environmental and Engineering Laboratory (INEEL) currently scheduled for the second and third week of July, 1998. It is an objective to rerun many of the same lines that were run as part of the Electromagnetics Integrated Demonstration (EMID) in 1995 at the Cold Test Pit to help us assess the relative performance of the new antennas

and transmitters over the same targets. We anticipate running at new sites as well. Assessments of these results will help guide our activities during the second and third years of this work. We anticipate that the emphasis will gradually shift to numerical modeling, data processing, interpretation, and visualization during the final two years, although improvements to the instrumentation will continue.

Other Access To Information

Reports and papers produced as part of the present work are:

Cui, T.J., and W.C. Chew, Efficient evaluation of Sommerfeld integrals for TM wave scattering by buried objects, J. Electromagnetic Wave Appl., Vol. 12, pp.607-657, 1998.

Cui, T.J., and W.C. Chew, Efficient method for the near-field detection of buried dielectric and conducting objects, Research Report, Electromagnetic Laboratory, University of Illinois at Urbana-Champaign, 1998.

Cui, T.J., and W.C. Chew, Fast evaluation of Sommerfeld integrals for EM wave scattering and radiation by three-dimensional buried objects, Technical Report, Electromagnetic Laboratory, University of Illinois at Urbana-Champaign, 1998.

Wright, D.L., Cui, T.J., and Chew, W.C., Progress on the very early time electromagnetic (VETEM) system, Proc. of the Seventh Internation Conference on Ground-Penetrating Radar (GPR'98), May 27-30, 1998, Lawrence, Kansas, (in press).

Additional information may be found in the References contained in the above papers and reports.

Spent Nuclear Fuels

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

Steven C. Marschman, Pacific Northwest National Laboratory

Peter E. Haustein, Brookhaven National Laboratory
James P. Cowin, Pacific Northwest National Laboratory
Thomas M. Orlando, Pacific Northwest National Laboratory
Theodore E. Madey, Rutgers, the State University of New Jersey

Research Objective

This project involves basic research in chemistry and physics aimed at providing information pertinent to the safe long-term dry storage of spent nuclear fuel (SNF), thousands of tons of which remain in water storage across the DOE complex. The Hanford Site K-Basins alone hold 2300 tons of spent fuel, much of it severely corroded, and similar situations exist at Savannah River and Idaho National Engineering and Environmental Laboratory. The DOE plans to remove this fuel and seal it in overpack canisters for "dry" interim storage for up to 75 years while awaiting permanent disposition. Chemically-bound water will remain in this fuel even following proposed drying steps, leading to possible long-term corrosion of the containers and/or fuel rods themselves, generation of H_2 and O_2 gas via radiolysis (which could lead to deflagration or detonation), and reactions of pyrophoric uranium hydrides. No thoroughly tested model is currently available to predict fuel behavior during pre-processing, processing, or storage. In a collaboration between Rutgers University, Pacific Northwest National Laboratory, and Brookhaven National Laboratory, we are studying the radiolytic reaction, drying processes, and corrosion behavior of actual SNF materials, and of pure and mixed-phase samples. We propose to determine what is omitted from current models: radiolysis of water adsorbed on or in hydrates or hydroxides, thermodynamics of interfacial phases, and kinetics of drying. A model will be developed and tested against actual fuel rod behavior to insure validity and applicability to the problems associated with developing dry storage strategies for DOE-owned SNF.

Research Progress and Implications

This report summarizes work after eight months of a three-year project.

Relevant oxide surfaces of UO_2, ZrO_2, and Al_2O_3 have been prepared and characterized by x-ray photoelectron spectroscopy. Measurements are being made of the desorption of water from these surfaces, using accurate thermal desorption methods to elucidate the effects of temperature on the surface-water interaction. Interfacial nuclear decay and radiolysis processes that either affect the structural integrity of relevant materials or evolve flammable gases have been studied on Al_2O_3 and ZrO_2 surfaces using intense radioactive sources with radiochemical tracer techniques. Processes for generating thin (0.1-mm) uranium oxide films have been developed using three different processes: metal sputtering; electrodeless plating; and thermal treatment of uranyl nitrate deposited from solution on tungsten. Such films have been characterized by electron microscopy, revealing in partially-nitrated specimens "shrink cracks" that may have profound implications for their chemical reactivity. A promising computational model of the effects of particle size and sample thickness has been developed and substantiated with experiments on MgO and TiO_2 powders. This will be applied to the analogous problems for SNF materials.

The breakdown of zirconia films (important to the integrity of Zr-alloy fuel-rod cladding) under extreme radiation conditions has been systematically studied using low-energy electron and photon bombardment of well-characterized ZrO_2 surfaces. These studies have clarified the mechanism of oxygen removal from such surfaces, which involves the ionization of shallow metal cation core

levels, followed by interatomic Auger decay resulting in the formation and rapid ejection of O+ ions. Simpler one- and two-electron processes can lead to the desorption of neutral and molecular oxygen. These complex processes are being studied using sensitive laser detection schemes to determine the exact quantum-state distributions of the species produced. Controlled radiolysis of water-covered ZrO_2 surfaces has begun, to clarify the interaction of adsorbates with secondary electrons, electron-hole pairs, and excitons near the surface. Preliminary experiments do not suggest enhancement of hydrogen production from adsorbed water, but this needs confirmation. A related study of the radiolysis of water adsorbed on a series of powdered oxides using 60Co gamma-irradiation reveals that the hydrogen yield from radiolysis can be significantly greater, approximately equal to, or significantly less than the yield from pure gas-phase water, depending on the specific oxide involved. Particularly interesting is that strong enhancement of the radiolysis (up to X 200) is seen only for a narrow range of oxide bandgaps. A mechanism has been proposed that accounts for these effects, based on the migration of excitons to the surface and their resonant coupling with the water adsorption complex.

Planned Activities

The thermal and electron-stimulated desorption kinetics of water from well-characterized UO_2 surfaces will be measured using a radiotracer techniques with tritiated water. The surface radiolysis studies with radioactive sources will be extended to uranium oxide systems. High-intensity 10-MeV femtosecond electron pulses will be used to simulate the effects of beta-ray and resulting cascades of lower-energy electrons. A final agreement on radiological protocols for the EMSL laboratory will allow UO_2 samples to be studied with the full array of instrumentation available there. The powder drying model will be tested against other oxides, including those of uranium. The radiation chemistry of zirconia will soon be extended to alumina and oxides of uranium. The influence of radiolysis on adsorbate materials will be clarified and these experiments will be extended to uranium oxides.

Flow Visualization of Forced and Natural Convection in Internal Cavities

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Research Objective

The objective of this research program is to understand the fluid physics when corroded spent nuclear fuel (SNF) elements are passivated by injecting treatment gases into a storage canister. By developing a reliable predictive technique for the energy, mass, and momentum transfer in the presence of surface reactions, transfer and storage systems can be efficiently and safely designed. The objective will be reached by using innovative flow visualization techniques and experimental measurements of the flow field to support computational models.

Research Progress and Implications

This report summarizes work completed after eight months of a three-year, collaborative project. A generic idealization of a combined drying and passivation approach has been defined, which represents a section of a vertical canister with baskets of SNF elements. This simulation includes flow phenomena that occur in canisters for high- and/or low-enrichment fuels. A steady flow of the passivation fluid is introduced at the bottom of the canister via a central tube from the top. Fluid flows through an array of holes in the perforated basket support plate then around the simulated elements and out the top. Dimensions and flow rates for the idealized situation correspond to those for typical drying canisters. Approximate calculations have identified the ranges of values of flow parameters needed to determine the flow regimes occurring in practice.

For effective passivation, a design aim would be controlled, high mass transfer rates to the fuel elements. These rates will depend on the flow pattern and turbulence levels in the vicinity of the elements. The fundamental flow features of the generic model have been identified as follows: 1) fluctuating velocity components in low Reynolds number turbulent flow in a tube; 2) turbulent transport and laminarization of a semi-enclosed, submerged impinging jet; 3) low Reynolds number flow through an array of holes; and, 4) decay of turbulence in flow around an array of elements. Available basic knowledge for these four fundamental topics is meager to non-existent.

Preliminary flow visualization experiments using dye and neutrally buoyant particles have been performed with scaled-down versions of the idealized canister. Two geometries of basket support plates, one with a 50% open area and the other with a 4% open area, have been used. With 50% open area, the flow pattern is comparable to that of a semi-infinite impinging jet with formation of a large vortex and entrainment and recirculation through the holes near the center. Upflow is primarily through the outer holes. With 4% open area, a large recirculation region occurs above the perforated plate, and a small recirculation zone forms below the perforated plate. It appears that the flow is circumferentially periodic. This observation implies that numerical predictions and detailed measurements can concentrate on a sector of the idealized geometry rather than the full cross section. Design of a half-scale experiment, using the INEEL Matched-Index-of-Refraction (MIR) flow system, has been initiated to measure velocity and turbulence fields.

Materials for an Individual Particle Tracking (IPT) 1/2-scale model to be built at OSU have been received. The design is virtually finished and construction will proceed in the early part of the summer. This model will be used as a proof-of-concept experiment, to provide a near realistic flow configuration to be examined with the IPT system. The computers, frame grabbers, cameras, and synchronization box have been checked, and we are moving on with the software development. The major thrust of the effort has been the development/porting of the imaging software from a DOS environment to Windows 95. This task is paramount to the integration/development of a new system. A list of key required features have been identified and about half of them have been successfully resolved. Once this task is complete, the bulk of the existing software for particle tracking can be easily ported. We expect a fully functional system under Windows 95 by late Summer/early Fall 1998.

The fully developed low Reynolds number pipe flow in the entrance tube has been modeled and numerical results have been obtained. Currently, the results are being reviewed and compared to existing experimental and/or numerical data to assess the numerical model. A comprehensive literature review has been completed in order to determine the proper form of the model for the low Reynolds number submerged jet impingement. Efforts are underway to select either previous experimental or numerical results to validate the numerical output. The validation will examine the ability of the turbulence models used within the code to predict correctly the impinging jet flow. Current efforts center on the review of the literature to find an appropriate benchmark. The flow through the perforated plate poses the greatest uncertainty for the modeling efforts. The uncertainty deals with the impact the array of holes will have on the turbulence levels on the inlet and outlet of the perforated plate. One must determine how important the upstream turbulence level is in determining the downstream turbulence levels. Without knowing this, it will be difficult to predict the mass transfer to the surface of the fuel elements, since turbulence levels impact mass transfer to the element surfaces.

Planned Activities

We will continue to develop methods to visualize flow in the presence of surface reactions. Some of the current techniques that we are investigating include chemical tracers, reacting dyes, fluorescent particles, and electrochemical surfaces. The initial experiment in the INEEL MIR flow system will concentrate on the fundamental problems of turbulent transport and laminarization in semi-confined flow of a low Reynolds number impinging jet using a new two-component Laser Doppler Velocimeter. These measurements should occur during the second year. By early Fall, the proof-of-concept experimental setup will be ready, and it is expected that the traversing Particle Tracking Velocimeter, aimed at developing the IPT, will be available during the third year. This capability will permit following individual particles (simulating motion of an oxidant) as well as determination of the three-dimensional flow field.

The perforated plate flow phenomena will be examined through the use of Direct Numerical Simulation (DNS) then the flow over the fuel elements will be analyzed. The approach to modeling the flow over the fuel elements will depend heavily on the DNS results. At present, a three-dimensional representative section of the model is being developed to examine the qualitative characteristics of the flow field. Once completed, these simulations will be compared to the experimental results.

Gamma Ray Imaging for Environmental Remediation

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Research Objective

The objective of this research is the development of high resolution germanium detector systems for direct imaging of spent nuclear fuels and fissile materials and Compton scatter imaging of large objects of arbitrary size. A small configuration of detectors shall be assembled to demonstrate the performance of such a system.

Research Progress and Implications

The efforts in this first year of a three year program have been focused on the design and procurement of a four detector array of germanium strip detectors. The basic detector is a 5 cm x 5 cm x 1 cm thick planar germanium detector with segmented anode and cathode. These segmentations are in the form of strips with a pitch of 2 millimeters. The strips on the anode side run orthogonal to the strips on the cathode side so that, in a gamma-ray interaction, the collection of electrons and holes on opposite electrodes produces signals which identify the interaction position in two dimensions. Each detector in the array has 25 anode contacts and 25 cathode contacts.

The detector array has been designed as a planar array providing 100 square centimeters of active area mounted in a single cryostat. To reduce electronics channel count, parallel strips from adjacent detectors are electrically joined together effectively making strips that are 10 cm long. In this configuration, 100 channels of electronics are required to readout the array.

In a related project, we are investigating processes to produce improved contacts for germanium strip detectors which would offer both more reliable extended use and the potential for finer strip pitch or position resolution. Investigating amorphous contacts, we have, to date, prepared two Ge test detectors. One was produced using n-type Ge and the other p-type Ge. The p-type detector has a Li diffused contact on one side while the n-type detector has a B ion-implanted contact. Amorphous contacts have been formed on the opposite side of each detector by RF sputtering. We are currently conducting a series of leakage current versus operating temperature measurements in order to determine the barrier heights of the amorphous contacts. The use of n and p type detectors will allow us to measure the electron and hole blocking behavior of the contacts respectively. This will provide important information on the nature of these contacts and will determine if double-sided strip detectors can be produced using only amorphous contacts.

Planned Activities

The germanium detector array will shall be delivered in December of 1998. Electronic preamps, provided by NRL, will have been installed. Operational testing will consist of connecting to a CAMAC/NIM data acquisition system consisting of shaping amplifiers, discriminators, and pulse height analyzers controlled by a computer. The detectors will be characterized for energy resolution and position resolution using laboratory radioactive sources, ^{241}Am and ^{137}Cs. In the Spring of 1999, coded aperture masks will be incorporated into the configuration to demonstrate direct imaging of phantoms and plutonium buttons.

The detector contact development will continue with test detectors fabricated with amorphous contacts deposited under different sputter conditions such as hydrogen concentration in the sputter gas. Also, both amorphous Ge and amorphous Si will be investigated as the contact material.

Direct Investigations of the Immobilization of Radionuclides in the Alteration Phases of Spent Nuclear Fuel

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Research Objective

In an oxidizing environment, such as in the proposed repository at Yucca Mountain, rapid alteration rates are expected for spent nuclear fuel. Laboratory-scale simulations have repeatedly shown that the dominant alteration products under repository conditions will be uranyl phases. There is an inadequate database that relates to the effects of the alteration products on the release of radionuclides, but this information is essential to provide a radionuclide release estimate. It is likely that many of the radionuclides contained in the fuel will be incorporated into the alteration products that form, potentially with a profound impact on the future mobility of radionuclides in the repository. Our objective is to characterize the incorporation of radionuclides into alteration products by synthesis of

uranyl phases doped with radionuclides, appropriate surrogate elements, or non-radioactive isotopes, followed by detailed phase characterization by diffraction and spectroscopic techniques. The research will permit a more realistic estimate of the release rates of the radionuclides from the near-field environment.

Research Progress and Implications

This report summarizes work after 8 months of a 3-year project. Our objective of investigating radionuclide incorporation in uranyl phases has required the development of synthesis techniques for various uranyl phases that are expected to form under repository conditions. We have synthesized and determined the structures of several uranyl phases that are new to science and that may be important alteration products under repository conditions. We have also undertaken the determination and refinement of the crystal structures of various uranyl phases that are likely to form under repository conditions. Other experiments include the investigation of the ion-exchange properties of uranyl phases under repository conditions.

Development of synthesis techniques

A major thrust of our research to date has been the development of synthesis techniques, with emphasis on obtaining crystals of sufficient size for complete characterization, including crystal structure determinations. Three basic synthesis techniques are being developed: (1) hydrothermal synthesis in Teflon-lined reaction vessels, (2) crystal nucleation and growth by diffusion in Si gels at room temperature, and (3) batch crystallization at room temperature. Efforts to date have provided the uranyl phases dehydrated schoepite $UO_3(H_2O)0.8\text{-}1.0$, uranophane $Ca[(UO_2)(SiO_3OH)]^2(H_2O)^5$, boltwoodite $(K,Na)[(UO_2)(SiO_3OH)](H_2O)1.5$, becquerelite $Ca[(UO_2)^3O_2(OH)_3]^2(H_2O)8$, ianthinite $[U_4+(UO_2)^4O_6(OH)^4(H_2O)^4](H_2O)^5$, and compreignacite $K_2[(UO_2)^3O_2(OH)_3]^2(H_2O)^7$, all of which are expected to form under repository conditions. Our experiments have shown that the crystallinity of the products is dependent upon pH, temperature, degree of saturation, and time. We have made significant progress in identifying the optimal conditions for the synthesis of each phase of interest. Our efforts to synthesize the Sr analogues of uranophane and becquerelite, and the Cs analogues of boltwoodite and compreignacite have provided a variety of uranyl phases, although crystals of a size suitable for structure characterization have not yet been obtained. Characterization of the run products is continuing using X-ray powder diffraction.

We have attempted to synthesize a Cs-Ba-Mo phase that has been found as a corrosion product on spent nuclear fuel in laboratory tests. This phase has proven to be difficult to synthesize, but recently we have obtained a Cs-Ba-Mo uranate phase that may be the same as the phase found on the spent fuel. Characterization of this phase is continuing.

Synthesis and structures of new uranyl phases

Our synthesis efforts have resulted in several uranyl phases that are new to science. These include the Sr analogue of the Pb uranyl oxide hydrate mineral curite, a Cs uranyl oxide hydrate, and a new polymorph of uranophane composition. Each of these phases are possible alteration products under repository conditions. We obtained excellent crystals of each of these phases, and have determined and refined the crystal structures of each, providing considerable new insight into the crystal-chemistry of uranyl phases in general, and especially those that contain Cs and Sr.

Determination of the structures of compreignacite and boltwoodite

Compreignacite has been identified as an alteration product in experiments on spent fuel. We have determined the crystal structure of compreignacite using natural crystals. This structure, which was previously unknown, contains sheets of uranyl polyhedra with K and H_2O in interlayer positions. Knowledge of the structure facilitates the prediction of radionuclide incorporation mechanisms in this phase. We have also determined the structure of a crystal of boltwoodite with Na-K solid-solution, and demonstrated the compatibility of the structure for radionuclide incorporation.

Discovery of ion-exchange properties of uranyl minerals

We have demonstrated for the first time ion exchange in single crystals of a uranyl mineral by replacing K^+ and Na^+ with Cs+ in the interlayer sites of boltwoodite, a common alteration product of spent fuel under laboratory conditions. These experiments were done with single crystals of natural boltwoodite, and ion exchange was demonstrated by crystal-structure determination. The ease of Cs exchange into boltwoodite has implications for the mobility of Cs in a repository containing spent nuclear fuel. Boltwoodite will likely form in close proximity to corroded spent oxide fuel, and is likely to be abundant. If Cs is in the water from which boltwoodite crystals nucleate and grow, boltwoodite will incorporate Cs directly into its structure, thereby inhibiting the release of radioactive Cs from the repository. In addition, contact of Cs-rich solutions with pre-existing boltwoodite may result in Cs exchange into the boltwoodite crystals, also reducing Cs mobility. However, subsequent interaction of Cs-poor solutions that contain other alkali metals with Cs-containing boltwoodite could liberate Cs by ion exchange and increase its mobility. Our work has also shown that it is likely that additional radionuclides can be exchanged into uranyl minerals, and this has important implications for the long-term evolution of a geological repository containing spent nuclear fuel.

Planned Activities

Synthesis of uranyl phases doped with radionuclides

During the next several months we plan to continue the development of optimal techniques for the synthesis of uranyl phases that are likely to form under repository conditions. During the second year of the project, and following complete characterization of these phases, we will investigate the incorporation of radionuclides into their structures by synthesizing radionuclide-doped phases. One phase that we consider to be a high-priority is dehydrated schoepite because it incorporates minor amounts of Np into its structure based upon corrosion experiments conducted on spent fuel. We will attempt to synthesize Np-doped dehydrated schoepite, and demonstrate this by XAS.

Ion exchange in uranyl phases

Our discovery of the ion-exchange properties of boltwoodite implies that ion exchange may be possible in many of the alteration phases that will form under repository conditions. We are continuing our investigations of ion exchange in several uranyl phases expected to form under repository conditions, with early emphasis on Cs, and with later work to include actinide elements. This will permit us to delineate the phases for which ion exchange is potentially important, and will aid in assessing the significance of ion exchange for estimating radionuclide mobility under repository conditions.

Other Access To Information

Burns, P.C. (sub.): The crystal structure of compreignacite, $K_2[(UO_2)^3O_2(OH)_3]^2(H_2O)^7$. Canadian Mineralogist.

Burns, P.C. (sub.): Implications of solid-solution in the structure of boltwoodite. Canadian Mineralogist.

Burns, P.C. & Hill, F.C. (sub.): Implications of the synthesis and structure of the Sr analogue of curite. Canadian Mineralogist.

Hill, F.C. & Burns, P.C. (sub.): Investigations of the crystal chemistry of uranyl oxide hydrates. IMA, Toronto (1998) (abst.).

Burns, P.C. (sub.): Topological aspects of uranyl mineral structures. IMA, Toronto (1998) (abst.).

Kim, C.W. & Wronkiewicz, D.J. (1998): Alteration phases of spent nuclear fuel. Missouri Academy of Sciences, 1998 Annual Meeting (abst.).

Radionuclide Immobilization in the Phases Formed by Corrosion of Spent Nuclear Fuel: The Long-Term Assessment

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Research Objective

This research program is designed to identify the long-term corrosion products of naturally occurring UO_{2+x} under oxidizing conditions as an analogue for corrosion of UO_2 in spent nuclear fuel. This work will identify the phases that form, the reaction path during their formation, their stability, and their ability to incorporate key radionuclides.

Research Progress and Implications

As of May 1998, this report summarizes work that has been completed during the first seven months of a 3 year research program. During this period, a post-doctoral fellow, F. Chen, has focused his efforts on the development of a theoretical basis for predicting the Gibbs free energies and enthalpies of formation of uranium (VI) phases. This is quite important, as these uranyl phases are the important alteration products that form during the corrosion of UO_2. The thermodynamic data base for these uranyl phase is extremely limited and often contradictory. Most previous efforts have been based on methods that sum, in stoichiometric proportions, the contributions of simpler constituent components to the ΔG^0_f of uranyl phases. Our approach for estimating the $\Delta G^0_{f,298}$ and $\Delta H^0_{f,298}$ of uranium (VI) phases is based on the observation that each type of coordination polyhedron has a set of well defined thermodynamic properties. In our analysis, the ΔG^0_f and ΔH^0_f of U(VI) minerals are considered to be the sum of oxide polyhedral contributions that were determined by multiple linear regression.

There is good agreement between the estimated and measured thermodynamic values for the minerals used in this model (Tables 1 and 2). Additionally, their natural occurrences confirm the potential of this approach as a tool in understanding and predicting the paragenesis and stability of U(VI) phases that form as a result of the alteration of uraninite and the UO_2 in spent nuclear fuel.

This approach offers the following advantages: (1) the structural component-summation technique provides improved accuracy relative to the oxide-summation technique if the coordination of the cation is considered; (2) the ΔG^0_f and ΔH^0_f may be estimated even though data for representative minerals in similar structural classes are not available because each type of cation polyhedron is considered to possess a set of well defined properties; (3) small errors in individual data of the reference phases can be reduced by multiple regression if the data base is large enough.

Although such an approach should not replace accurate experimental determinations, this method can be used in the absence of experimental data to infer the stabilities of U(VI) phases in various systems. Additionally, the estimated thermodynamic data can be used to suggest important pathways for long-term U(VI) phase transformations, and this can serve as a guide for future experimental work. Finally, results obtained by this method can be immediately improved as more accurately determined structures and thermodynamic data for U(VI) minerals become available.

Table 1. Comparison of measured and predicted $\Delta G^0_{f,298}$ values for phases used in the model and the associated errors.

U(VI) phases	Measured (kJ∑mol^{-1})	Predicted (kJ∑mol^{-1})	Absolute residuals (kJ∑mol^{-1})	Relative residuals %
$[(UO_2)_8O_2(OH)_{12}]\cdot 10H_2O$	-13092.0±6.8	-13122.9	30.9	0.24
β-$UO_2(OH)_2$	-1398.7±1.8	-1399.3	-0.6	0.04
$UO_3\cdot 0.9H_2O$	-1374.6±2.5	-1375.6	1.0	0.07
$Na_2U_2O_7$	-3011.5±4.0	-3013.0	1.5	0.05
$Na_4UO_2(CO_3)_3$	-3737.8±2.3	-3739.8	2.0	0.05
UO_2CO_3	-1563.0±1.8	-1562.3	-0.67	0.04
$BaUO_4$	-1883.8±3.4	-1886.6	2.8	0.15
BaU_2O_7	-3052.1±6.7	-3048.8	-3.3	0.11
$UO_2(NO_3)_2\cdot 6H_2O$	-2584.2±1.6	-2583.8	-0.4	0.01
$UO_2(NO_3)_2\cdot 3H_2O$	-1864.7±2.0	-1862.9	-1.8	0.09
$UO_2(NO_3)_2\cdot 2H_2O$	-1620.5±2.0	-1622.6	2.1	0.13
$UO_2SO_4\cdot 3.5H_2O$	-2535.6±1.8	-2537.1	1.5	0.06
$UO_2SO_4\cdot 3H_2O$	-2416.6±1.8	-2416.9	0.3	0.01
$UO_2SO_4\cdot 2.5H_2O$	-2298.5±1.8	-2296.8	-1.7	0.08
$(UO_2)_2\ SiO_4\cdot 2H_2O$	-3655.7±7.6*	-3651.8	-3.9	0.11
$Na(UO_2)(SiO_3OH)\cdot 1.5H_2O$	-2844.8±3.9*	-2838.8	-6.0	0.21
$Na_2\ (UO_2)_2(\ Si_5O_{13})\cdot 3H_2O$	-7993.9±9.6*	-8000.5	6.6	0.08
$Ba(UO_2)_6O_4(\ OH)_6\cdot 4H_2O$	-9387.0±17.1*	-9370.0	-17.0	0.18
Average				0.095

*calculated based on the solubility data provided by Nguyen et al. (1992), Casas et al. (1997b) and Vochten and Haverbeke (1990); measured $\Delta G^0_{f,298}$ values for other phases are from Grenthe et al. (1992).

Table 2. Comparison of measured and predicted $\Delta H^0_{f,298}$ values for phases used in the model and the associated errors

Uranyl phases	Measured (kJ∑mol^{-1})	Predicted (kJ∑mol^{-1})	Absolute residuals (kJ∑mol^{-1})	Relative residuals(%)
β-$UO_2(OH)_2$	-1533.8±1.3	-1531.2	-2.6	0.17
γ-$UO_2(OH)_2$	-1531.4±1.3	-1531.2	-0.2	0.01
UO_3∑$0.9H_2O$	-1506.3±1.3	-1509.3	3.0	0.20
β-Na_2UO_4	-1884.6±3.6	-1885.5	0.9	0.05
Na_4UO_5	-2456.6±1.7	-2458.7	2.09	0.09
$Na_2U_2O_7$	-3203.8±4.0	-3197.7	-6.12	0.19
Li_2UO_4	-1968.2±1.3	-1973.1	4.87	0.25
Li_4UO_5	-2639.4±1.7	-2633.9	-5.5	0.21
$UO_2(NO_3)_2\cdot 6H_2O$	-3167.5±1.5	-3167.9	0.4	0.01
$UO_2(NO_3)_2\cdot 3H_2O$	-2280.4±1.7	-2277.7	-2.7	0.12
$UO_2(NO_3)_2\cdot 2H_2O$	-1978.7±2.0	-1981.0	2.3	0.12
$UO_2SO_4\cdot 3.5H_2O$	-2901.6±0.8	-2901.7	0.1	0.005
$UO_2SO_4\cdot 3H_2O$	-2751.5±4.6	-2753.4	1.9	0.07
$UO_2SO_4\cdot 2.5H_2O$	-2607.0±0.9	-2605.0	-2.0	0.08
Average				0.11

Note: measured $\Delta H^0_{f,298}$ values are from Grenthe et al. (1992).

Planned Activities

During the next year, our program will focus on four areas: **1.** Detailed analysis of natural samples to identify the principal phases and their proportions as a function of geochemical conditions and reaction progress. **2.** Analysis of uranyl phases for their trace element content, that is a determination of the fate of impurity elements that are released during matrix dissolution of the UO_2. **3.** An evaluation of the long-term stability of uranyl phases under oxiding conditions. **4.** Comparison to theoretical calculations of phase stability to actual natural occurrences of these uranyl phases.

Wolf-Broido

Miniaturized, Optical-Based Sensors for Extreme Environments

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Research Objective

To capitalize on the rapid progress in optoelectronics and semiconductor microfabrication technologies to produce miniature optical spectrometers to enable the development of miniature optical sensors for *in situ* characterization of wastes in extreme environments. Specifically, we propose to develop a micro-spectrometer based on a novel correlation spectrometer coupled with high brightness, semiconductor LED sources and semiconductor detectors. By tuning the operating wavelength to match the spectral signatures of different chemical species the micro-spectrometer concept can be adapted to the detection of a wide variety of organic and inorganic compounds.

Research Progress and Implications

This report summarizes work after 2 years of a 3 year project. We have developed an algorithm that allows the calculation of diffraction grating profiles for which multiple wavelengths can be diffracted at the same angle. This development extends the application of diffraction optics from spatial domain optical processing into the spectral domain. This algorithm can be used to define novel diffraction gratings that synthesize the spectra of molecules. Spectra of chemical species that are difficult or dangerous to handle or that exist for a very short period of time can be synthesized. Such a grating can then be used in a correlation spectrometer to provide a simple monitor for such species. Conventional correlation spectroscopy passes light through a gas volume to be sampled and then through a reference cell containing the target species. The spectrum of the reference species is modulated using pressure or a large electric field. If the spectral features from the reference cell overlap those from the sample volume, a modulated output occurs. If there is no overlap, then there is no modulation of the output. The reference cell can be replaced by the novel grating that generates the desired synthetic spectrum and the wavelength modulated by rocking the grating. Such correlation spectrometers will be simple, inexpensive monitors for wide array of dangerous chemical species including poisonous agents, transient species, and corrosive species.

Gratings have been fabricated that reproduce the absorption spectrum of HF, toluene, MIBK, and kerosene. The gratings are reactive ion etched on single crystal silicon wafers using a 4 mask level sequence that allows 16 discrete levels for the grating elements. After fabrication the silicon wafer is coated with gold to form a reflection grating. Each grating element is about 5 microns wide. The number of grating elements determines the resolution of the diffracted spectrum. The spectral content of the diffracted beam has been measured for HF. No anomalous features are observed outside of the HF band. These results confirm the concept of multi-periodic gratings for synthesizing molecular spectra and agree well with the calculated grating response. A modulation factor of 80nm/(°) was measured for the HF grating which indicates modulation of the synthetic spectra will be easy to do and that modulation over a wider spectral range will be possible than is possible with a conventional correlation spectrometer.

A numerical study was performed to understand the effect of etch-depth errors on the fidelity of the spectra synthesized by the diffractive optic. It found that the performance of diffractive elements is not strongly affected by realistic depth errors (+/- 10%). Fortunately, with modern microlithographic techniques, it is relatively straightforward keep the depth errors below 10%. Model calculations were also performed to explore the effects of the number of etch levels on the performance of the gratings. These calculations showed that an 8 level phase grating is almost indistinguishable from a 16 level grating at reproducing spectra. Even 2 level gratings do an adequate job of reproducing the

spectra. The major effect of reducing the number of etch levels is a significant reduction in the efficiency of the gratings.

We have begun to develop techniques for utilizing rigorous vector diffraction theory in the design of new diffraction gratings. The current design algorithm utilizes a scalar theory that breaks down as the dimensions of the structure approach the wavelength of light. While it appears to perform adequately, the more accurate theory will allow us to determine if some of the discrepancies observed between the fabricated grating spectral response and the calculated synthetic spectra are due to modeling deficiencies rather than fabrication errors. The boundary element method (BEM) is simple to implement, and is appropriate for our metal, coated optics. We have developed computer code to apply the BEM to the design of spectral holograms.

We have also developed a computer model to simulate the performance of correlation spectroscopy for several important hazardous gases such as HF, HCl, HBr, HI and HCN. Using the computer model, we have found that the gases, HCl, HBr and HI can be detected at concentrations less than 1 - 10 parts per billion. Sensitivity is limited only by the availability of low noise detectors and bright sources. For HF and HCN, we have found concentrations of 1 - 10 parts per million are readily detectable. The reason for the lower sensitivities of these two gases is the spectral interference from water, which is present at the 0.1% level in the atmosphere.

Improved broadband LED infrared sources for use in chemical sensing applications have been demonstrated. We have used the semi-metal properties of a p-GaAsSb/ n-InAs heterojunction as a source for injection of electrons into the active region of InAsSb infrared emitters. The use of an internal electron source enables us to consider alternative LED designs that would not be feasible with conventional, bipolar devices. We have grown a 2 stage/2 color LED where the Sb mole fraction of the active regions differs by 0.03 to allow emission from each stage to be observed. Two overlapping peaks that increase the bandwidth of the LED are observed for this device. LED emission has been observed at 300K, 4 μm with = 100 μW peak power.

Planned Activities

The focus for FY98 is demonstration of a correlation spectrometer for chemical sensing using these new diffraction gratings. The design will be optimized to make the optical package as small and portable as possible. A design algorithm utilizing the more accurate vector diffraction theory will be developed and results compared to the current scalar theory. Grating design will be optimized to maximize performance while minimizing fabrication costs and difficulty.

Other Access To Information

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Automation of Radiochemical Analysis by Flow Injection and Sequential Injection Methods

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Research Objective

The remediation of radiochemically contaminated sites and processing of stored wastes into stable waste forms will require characterization procedures throughout all phases of these activities. Unless methods are found to do these analyses rapidly and precisely, the analytical process will be so time-consuming and costly that it will greatly slow the cleanup process. Alternatively, the process might move forward without all the needed analysis and, therefore, without a firm scientific basis for decisions. In the future, real time analytical methods will be needed for process control when waste processing plants are built and operated.

The objective of this project is to develop new automated radioanalytical techniques in order to meet these characterization needs. The new methods will provide improved precision, consistent analytical protocols, reduced worker exposure to toxic and/or radioactive samples, greater sample throughput, reduced costs, and reduced secondary waste generation.

Flow injection (FI) and sequential injection (SI) methodology are being used to automate sorbent extraction radiochemical separations processes and deliver the sample to the detector or fraction collector. Radiochemical separation chemistry is being investigated with regard to issues that must be addressed to successfully automate such methods for analytical purposes, including analyte recoveries, separation from interferences, reproducibility, rigorous control of speciation, kinetics of on-line reaction chemistry, characterization of separation materials, and the effects of complex sample matrices. Novel methods are being developed for renewing separation columns on-line by moving, capturing, and releasing polymer beads. Multiple detection approaches, i.e. both radiation counting and atom counting methods, are being used for the quantification of separated radionuclides. The primary focus is on radiochemical methods as they apply to the analysis of aged nuclear wastes.

Research Progress and Implications

This summary describes progress as of 2 years into a 3-year project.

Instrumentation and methodology. We have greatly improved the instrumentation for doing automated radiochemical analysis, and developed new fluid handling methodologies optimized for radiochemical separations. Conventional FI and SI techniques operate on much smaller solution volumes and simpler procedures than those required for radiochemical separations. Our present instrumentation requires minimal maintenance or calibration, is reliable, is more precise, and has a graphical user interface for method development or implementation. These features should facilitate operation by potential users.

Radiochemical Separations: The heart of this program is the automation of radiochemical separations using sorbent extraction techniques. In our first phase, we have focused on separations using fixed columns of selective sorbent extraction resins operating by complexation and/or ion exchange. We have developed automated procedures for: Sr-90 separation and quantification; Tc-99 separation and quantification; separation of gross actinides from sample matrices; separation of transuranics from the sample matrix and from high uranium-containing matrices; and separation of Am and Pu. These cover the key radionuclides relevant to nuclear waste that typically cannot be determined by direct analysis (gamma counting), and require separations prior to quantification.

Typical sorbent extraction separations are accomplished through controlled differences and sudden changes in capacity factors (retention) for the radionuclides of interest and interfering species. These differences in retention are provided through selective interactions between sample, sorbent

material, and eluent solution. In the case of the actinide separations, on-column redox chemistries are used to facilitate the separation and enhance its selectivity. These processes are achieved through programmed delivery of various eluents and reagents.

The FI/SI platform for very precise automated fluid handling coupled to on-line detection has proven to be a useful platform for investigating as well as automating radiochemical separations. We have found that existing manual procedures for sorbent extraction separations can seldom be directly implemented in an automated system without considerable investigation. We have developed new or modified procedures for sorbent extraction radiochemical separations in order to optimize performance in an automated format.

Our second phase of separations research involves use of renewable separations media. We have developed a unique approach for packing a separation column on-line, using it for a separation, and discarding the separation material, all under computer control. This approach has been demonstrated for the analyses of Sr-90, Tc-99, and Am-241. The renewable separation approach eliminates problems with carryover of activity from one sample to the analysis of a subsequent sample. In addition, the instrument can be used for a variety of radiochemical analyses, loading the appropriate separation material and using appropriate reagents, selected under computer control, for the desired separation.

Detection: We have investigated and characterized on-line flow through liquid scintillation detection in detail as it applies radiochemical separations, including a new stopped-flow technique. Surprisingly, stopping the flow for longer counting times actually improved sample throughput! This result was achievable because our automated instruments can process the next sample while the current sample is being counted. We have initiated studies in using ICP-MS detection in combination with our automated separations.

Planned Activities

During the final year of this project, we are completing investigations of separations, chemistries and materials, coupling selected separations to ICP-MS detection, and development of new radiation counting detectors specifically for use with our automated analyzers. Ultimately we will investigate the possibility of integrating separation and detection operations in a single compact unit.

Other Access To Information

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"Sequential Injection Renewable Separation Column Instrument for Automated Sorbent Extraction Separations of Radionuclides," O. Egorov, M. J. O'Hara, J. W. Grate, and J. Ruzicka, submitted.

We have been invited to write an A-pages article for Analytical Chemistry.

Surface Chemistry at Subsurface Basalt

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Research Objective

The goal of this program is to investigate the sorption and degradation chemistries of chlorinated organics on basalt surfaces as it pertains to their fate and transport in fractured basaltic aquifers. The approach taken in this program is unique in that the sorption chemistry is being interrogated directly using a number of surface analytical techniques (such as secondary ion mass spectrometry (SIMS), scanning electron microscopy/wavelength dispersive x-ray spectroscopy (SEM/WDS), x-ray photoelectron spectroscopy (XPS), Raman and infrared spectroscopies). The results of this work are expected to provide direct information on the chemical reactivity of the basalt surface, which will provide insight into the mechanisms by which chlorinated organics are sequestered and/or degraded at the basalt surface.

Research Progress and Implications

This report summarizes work after 2 years of a 3-year project. This work has been accomplished through collaboration with the University of Arizona (Dr. Jeanne Pemberton), Idaho State University (Dr. Michael McCurry), Montana State University (Dr. Recep Avci), and INEEL - Subsurface Science Program (Dr. Bob Smith) and Environmental Management Science Program (Dr. Rick Colwell).

Initial work involved chemical characterization of the basalt surfaces using SIMS, SEM/WDS, and petrographic microscopy. These characterization experiments of mineral separates taken from the basalt suggest differences in the mineralogy comparing the surface and the bulk. Specifically, the plagioclase separates also show some iron-containing surfaces phases which are identified as pyroxene. The olivine phases show some iron/aluminosilicate containing phases which have been also been identified as pyroxene. The bulk analyses of these same separates indicated only trace amounts of pyroxene present. These results were important in interrogating the reactivity of the separates and interpretation of the surface chemistry.

We have utilized a SIMS microprobe at Montana State University to collect chemical images of the basalt surface. Due to the complexity of the SIMS imaging data, a method was developed to manipulate the data. A major part of this process is a program called SIMageS which statistically groups elements allowing identification of the mineral phases on the surface. This method is providing a means for us to investigate adsorption chemistry of intact basalt.

Prof. Mike McCurry and his graduate student David Bates have provided mineral separates of plagioclase, olivine, and iron titanates from TAN basalt. Bates is working on characterizing the Fe chemistry and TCE (trichloroethylene) reactivity as part of his thesis.

Prof. Jeanne Pemberton and her graduate student Steve Ringwald are using a combination of Raman and infrared spectroscopies to look at adsorbates on model mineral surface as well as adsorption of chlorinated compounds at the basalt mineral separates provided by the ISU group. This work has indicated very weak interaction of the TCE with the surface of plagioclase and olivine.

TCE reactivity studies, which involve aqueous TCE solutions and various basalts and iron oxides, are currently underway. Both surface analysis and analysis of the aqueous solution will be performed. The preliminary results of these experiments indicate that Fe(II) containing samples, such as FeO, $FeTiO_3$, and olivine will dechlorinate the TCE in aqueous solution under anaerobic conditions.

Planned Activities

During the final year of funding, the TCE reactivity studies will be completed. Kinetic and surface reactivity information will be generated. Interrogation of the surface will include the use of a newly designed cold-probe which will minimize evaporation of the volatile chlorinated organics from the surface of the basalt and related minerals under the vacuum conditions of the SIMS experiments. These data along with the molecular spectroscopy data will be interpreted in order to identify adsorption and/or degradation mechanisms of TCE at mineral surfaces.

Other Access To Information

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Submitted papers

1. "Raman and Infrared Spectroscopic Characterization of 2- and 4-Picoline Sorption to Silica as Model Pollutant-Soil System", S. C. Ringwald, J. E. Pemberton, J. C. Ingram, J. Environ. Sci. Tech., submitted.

Related work

Abstracts describing surface chemistry and instrumental development work accomplished by the SIMS research team at the INEEL is accessible at the following web page: **es.epa.gov/techinfo/research/newtech/pesims/abstracts.html**.

Improvement of Cadmium Zinc Telluride Detectors for Use in a Gamma-ray Imaging Spectrometer System for the In Situ Characterization of Underground Waste Tanks

Ralph B. James, Sandia National Laboratories

John M. Van Scyoc III, Sandia National Laboratories

Research Objective

There is a need for *in situ* characterization of the composition of wastes contained in underground storage tanks at a variety of DOE sites to allow for the application of safe and efficient remediation activities. Current methods rely on core sampling and laboratory analyses, which is an expensive and time-consuming process, as well as having the potential for exposure of personnel and creating secondary waste. This project focuses on the development of a new tool for *in situ* characterization. The primary element of this tool is a novel cadmium zinc telluride (CZT) gamma-ray imaging spectrometer. The gamma-ray spectrometer allows for the identification of waste constituents from their unique radiological features, either through their intrinsic emissions, or through external

excitation and subsequent emissions. The imaging function of the detector allows for the spatial mapping of the waste homogeneity by imaging liters of material with milliliter resolution. The fundamental enabling technology for this characterization tool is the CZT detector, as these semiconductor detectors are capable of operating in the extreme environments found in waste tanks — high temperatures, high radiation levels, and chemical harshness — while providing good spectroscopic capabilities. The primary factor inhibiting the engineering of the characterization system is the limitations of existing CZT detectors. These problems are caused by imperfections in the underlying materials properties, and can be overcome by improvement therein. The main objective of this project is to determine the specific factors limiting CZT detectors, and to implement improvements in the growth and processing technology to minimize these problems. The intended accomplishment of this project is the demonstration of a new capability for the spatial characterization of the radiological and elemental constituents of wastes stored in underground tank; the end product will be the components necessary to develop and implement an *in situ* waste characterization system.

Research Progress and Implications

As of the second year of this three year project, progress has been made in the understanding and improvement of CZT crystals for large volume detectors. Specific accomplishments include the benchmarking of current CZT materials and detectors from the major U.S. suppliers, and the coupling of a variety of material characterization techniques with device evaluations to identify the material deficiencies most limiting detector performance. High-resolution x-ray diffraction and topography measurements have revealed the highly mosaic structure of CZT crystals. Room-temperature photoluminescence mapping has revealed the variation of the alloy composition on the order of device dimensions and the effects of crystalline strains on carrier traps. Thermoelectric emission spectroscopy and related measurements have been used to identify the dominant trap levels, and their likely sources. Methods for fabricating detectors have been developed, and the effects of these processes on the materials properties and detector operation have been determined. Spatially-resolved measurements have been particularly effective at revealing the detailed source of device failures. Large scale alpha particle mapping has been used to show the regions and fraction of CZT boules that can produce specific grades of spectrometers and imagers. High resolution gamma-ray mapping has revealed that the overall performance of fabricated detectors is degraded in some cases by a very small region of bad material and in other cases by a large portion of poor material. These accomplishments have both enhanced the general body of knowledge on wide bandgap semiconductor nuclear radiation detectors and improved the availability of large volume CZT detectors for many DOE applications, including some that were previously unattainable. Environmental monitoring and remediation and nuclear materials monitoring capabilities are particularly improved.

Planned Activities

The third year of the project focuses on determining and improving the operating environmental limits for CZT detectors, continuing improvements in crystal growth and device fabrication techniques, fabrication of prototype spectrometers and imaging arrays, and development of instrument data acquisition and analysis methods.

Other Access To Information

The following are selected recent publications connected with this work.

H. Hermon, M. Schieber, N. Yang, R. B. James, N. N. P. Kolesnikov, Y. N. Ivanov, V. Komar, M. S. Goorsky, H. Yoon, J. Toney, and T. E. Schlesinger, “Study of Homogeneity of Cadmium Zinc Telluride Detectors”, in Semiconductors for Room Temperature Radiation Detector Applications II, Vol. 487, edited by R. B. James, T. E. Schlesinger, P. Siffert, W. Dusi, M. R. Squillante, M. O’Connell and M. Cuzin (Materials Research Society, Pittsburgh, PA, 1998), p. 223.

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EM/ER Project: Investigation of Groundwater Flow Paths in Fractured Aquifers Through Combined Inversion of Strontium Isotope Ratios and Hydraulic Head Data

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Dipak Sahoo, University of Illinois at Urbana-Champaign
Christine Doughty, Lawrence Berkely National Laboratory
Don DePaolo, Lawrence Berkely National Laboratory
Travis L. McLing, Idaho National Engineering and Environmental Laboratory
Robert W. Smith, Idaho National Engineering and Environmental Laboratory

Research Objective

The goal of this project is to find zones of preferential groundwater flow using $^{87}Sr/^{86}Sr$ isotope ratio measurements and hydrologic inverse methods employing fractal geometry concepts. These methods are being applied in a study of the Snake River Plain aquifer (SRPA) in and near the Idaho

National Engineering and Environmental Laboratory (INEEL) and yield important groundwater flow information.

Research Progress and Implications

This project has been funded for two years by the EM/ER Pilot Collaborative Research Program and is currently in its final year. Groundwater samples were collected from USGS monitoring wells, irrigation wells, and various other wells accessing the SRPA in and near the INEEL. Some of the wells sampled were in the region just southwest of the INEEL where access is difficult and samples are rarely taken. Over fifty $^{87}Sr/^{86}Sr$ analyses, over sixty ICP-MS analyses (for Na, Ca, Mg, K, Li, AL, Si, Mn, Fe, B, P, Sr, Ba, and U concentrations at USGS Menlo Park) and twenty oxygen isotope analyses were completed and combined with previous analyses done by the USGS. The results strongly suggest the existence of fast and slow flow zones in the central and southern areas of the INEEL, as described below. A numerical model was constructed to simulate the geochemical evolution of groundwater in these zones, and has been used to invert the data and arrive at quantitative constraints on groundwater flow.

Both ^{87}Sr and ^{86}Sr are stable isotopes, and natural variations in $^{87}Sr/^{86}Sr$ exist because ^{87}Sr is produced by radioactive decay of ^{87}Rb (half life: $48.8x10^9$ years). Thus, $^{87}Sr/^{86}Sr$ ratios vary in rocks depending on their Rb contents and history. The basaltic rocks of the SRPA have relatively low $^{87}Sr/^{86}Sr$ ratios (e.g., 0.70700), while waters entering the aquifer from areas to the north have a relatively high $^{87}Sr/^{86}Sr$ ratio (e.g., 0.71200). Chemical interaction between water and host materials tends to change the $^{87}Sr/^{86}Sr$ ratio along the path of flow whenever the added solute's $^{87}Sr/^{86}Sr$ ratio is different from that of the Sr already in solution.

The data, shown in the figure, indicate a zone of high $^{87}Sr/^{86}Sr$ groundwater in the north and northwestern areas of the INEEL, where northern tributary groundwater systems and surface water streams enter. Groundwater from these areas is apparently funneled into a relatively narrow, south-trending preferential flow zone that runs through the southern boundary of the INEEL. This high isotope ratio zone is flanked by zones of lower $^{87}Sr/^{86}Sr$. These are zones of slower groundwater flow where longer contact between water and the low $^{87}Sr/^{86}Sr$ basalt decreases the groundwater isotope ratios (though part of the gradient to the east is due to groundwater mixing). A set of archive samples was shipped to M. Murrell and R. Roback at LANL for a $^{234}U/^{238}U$ isotope study and a strikingly similar pattern emerged in their data. Thus, two complementary radiogenic isotope data sets produce similar results.

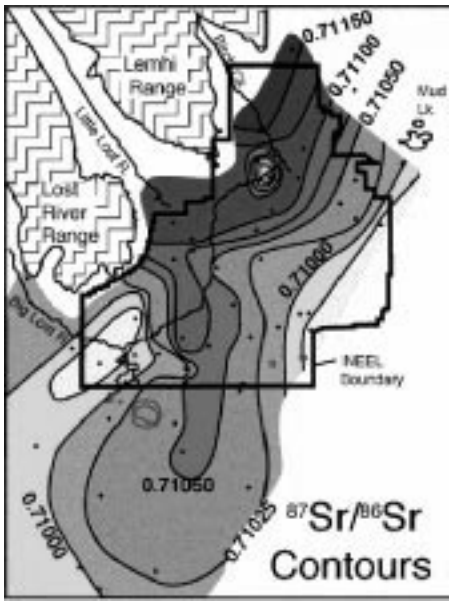

Figure 1

Solute concentrations might be expected to yield the same information as the isotope ratios with lower analysis costs. However, the patterns in the concentrations are not as coherent and do not correlate well with each other. There is a fundamental difference between isotope ratios and concentrations that makes the isotope ratios better indicators of groundwater residence time. The concentration of any dissolved species changes according to the difference between solute gains due to dissolution and ion exchange and solute losses due to precipitation and ion exchange. In contrast, solute $^{87}Sr/^{86}Sr$ ratios are always forced toward the ratio of dissolving or exchanging minerals. Thus, $^{87}Sr/^{86}Sr$ and other radiogenic isotope ratios are well suited as naturally occurring groundwater tracers, and should be considered a critical component of many hydrochemical data suites.

A major goal of this study is to interpret the $^{87}Sr/^{86}Sr$ data and available hydraulic head data quantitatively through the use of groundwater flow and transport models. A numerical model was constructed that simulates the evolution of Sr isotope ratios in the aquifer, using the 2-D transport code SUTRA. This model has been used to place constraints on the sizes and relative velocities of low and high transmissivity zones. Work with the model is ongoing.

The SRPA data set demonstrates the strengths of $^{87}Sr/^{86}Sr$ as a natural tracer of groundwater flow, and provides information about regional scale groundwater flow specific to the INEEL area. This is especially important in light of the geological complexity of the SRPA, which is hosted by fractured basalts with complex flow patterns.

Planned Activities

Three tasks remain in the project. The first is to complete the modeling of the Sr isotope data and hydraulic head data using a zone-based inversion scheme. In this method, boundaries of zones are chosen and the inversion finds best-fit values for the transmissivities of the zones. The second task is to complete and use inversions based on iterated function systems (IFS) to invert the data. This method does not require the user to impose zones on the system and is thus potentially more robust. The final task is to consider the potential for use of these methods at Oak Ridge and Hanford.

Near Infrared Detection Methods for Complex Mixtures

Donald Lucas, Lawrence Berkeley National Laboratory

David Littlejohn, Lawrence Berkeley National Laboratory

Research Objective

We are studying the spectroscopy for a fiber optic probe system that uses near-infrared (NIR) light and radiation resistant fibers and optics to determine the water, polyatomic ions, metals, and total organic carbon in complex waste mixtures. We are focusing on the liquid portions of the waste in the supernate or the interstitial saltcake liquid. The NIR probes offer the promise of near real-time measurements, spatial resolution on the order of centimeters, and good sensitivities.

Research Progress and Implications

This report summarizes work after two years of a three year project. Our research focuses on the spectroscopy of complex liquid mixtures using the absorption bands of water and other compounds,

such as hydrocarbons and polyatomic ions, in the near-infrared region (1 to 4 μm) of the spectrum. We are studying surrogate mixtures in the laboratory, identifying appropriate conditions for quantitative measurements, producing spectral calibration libraries, and fabricating and testing different sensors that can probe the components found in tank wastes.

The effects of various compounds on the water spectrum in the near-IR are investigated using various chemometric techniques such as partial least squares (PLS) analysis. Four component mixtures were measured with a precision error of 0.06 M for $NaNO_3$ and $NaNO_2$, 0.006 M for Na_3HEDTA, and 0.009 M for Na_2CO_3, using a 1 mm path length, 8 cm^{-1} resolution, and approximately 1 minute collection time in the 9000-5400 cm^{-1} region. We also used NIR to determine the total organic carbon (TOC) content in aqueous solutions. Samples containing Na_4EDTA, Na_3HEDTA, acetone, and tert-butanol were prepared with a total organic carbon concentration of between 2 and 7 %. NIR spectra gave good correlations ($R^2 = 0.9811$) between the TOC concentration and their NIR absorption; UV spectra of the same samples, measured at 252 nm using a diode array UV spectrometer, had a worse fit.

We are developing sensors to use in the field. Evanescent wave measurements are made by removing the cladding from a section of the fiber, and placing the bare fiber in contact with the sample. We are investigating different fiber configurations by modifying the fiber shape where it contacts the sample. Tapering, notching, or bending the fiber sensor significantly increases the sensitivity compared to a straight fiber, but tends to reduce its transmission, causing an increase in noise. We are searching for optimum fiber configurations by systematically varying the shape and size of the sensor region.

Several heavy metal-EDTA components are being studied that are excellent sensor-related chemical models for tank waste species. Structurally-documented, experimental heavy metal ion/water models have been synthesized for observing the effects of differently bonded water molecules; this makes it easier to correlate water band assignments in the infrared. Experimental models of heavy metals/organics [Fe/Co-EDTA] have been prepared that consist of homogeneous solid phases that are chemically heterogeneous. Infrared studies successfully assigned many infrared modes to chemical models of metal ion-organics in the solid phase; water modes have been shown to be very variable as a function of composition and structure. Synchrotron-based infrared spectroscopy has been used to distinguish different forms of chromium assimilated and altered by bacterial forms that are present in the Hanford tank farm area. CaF_2 phases have been prepared which are near-infrared inactive, Raman active, and fluorescent active with metal ion probes; these provide a sampling surface that can be used to detect heavy metals.

The effects of light scattering on absorption spectra are being explored using the hydrolysis of $FeCl_3$, which grow to produce cigar-shaped particles. At first, the resulting turbid suspension of β-FeOOH particles exhibits Rayleigh scattering ($\propto \nu^4$). At later times, the scattering increases strongly as the particles flocculate, becoming proportional to ν^n, with the *n* decreasing to values as small as 1. These results produce an analytical expressions that permits an accurate subtraction of scattering effects in the NIR.

Planned Activities

In the next year of our research, we plan to continue research on all aspects of the project described above, identifying and developing near- and mid-infrared methods that could be used to characterize tank wastes. We will continue using multivariate methods to quantify complex mixtures, and extend these methods to other optical configurations. We intend to initiate investigation of fiber-based sensors for studying subsurface applications, and explore the use of surface enhanced infrared absorption (SEIRA) to increase sensitivities. We will obtain additional infrared spectra using synchrotron infrared facilities at the Advanced Light Source (ALS). The assignment of full-range infrared spectra of heavy metal-organic-water systems based on structural data will continue, and infrared studies of reactions involving surrogate wastes, similar to those of the Fe-EDTA studies, will be conducted. Numerical and analytical modeling of the scattering results will be used to clarify under what conditions a simple power law for scattering is relevant for strongly scattering aggregates/gels. We will also examine the use of sapphire fibers to extend the spectral range of the sensors into

the mid-infrared, and test novel configurations for sampling the gas phase molecules in equilibrium with the liquid mixtures.

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Electrochemically Transformable Extraction Phases for the Separation of Critical Metal Ion Constituents in High Level Wastes

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Research Objective

Remediation of the large volumes of high level wastes (HLWs) throughout the U. S. Department of Energy laboratory complex requires the separation of radioactive materials into high and low level waste streams. Reclamation also dictates minimization of the volume of the high level waste stream to reduce long term storage costs. The performance of existing separation processes (e.g., the lack of specificity for cesium in the presence of a huge excess of sodium), however, do not always adequately address these needs. This program is exploring novel strategies for the separation of the radioactive components (e.g., cesium, strontium, neptunium, americium, and curium) in HLWs using redox transformable ligands. The aim is to exploit the unique capabilities of new types of metal ion selective ligands that incorporate redox transformable moieties as part of the binding site architecture. For example, we are preparing a series of metal-ion selective crown ether chelates (CEs) that are immobilized onto a carbonaceous chromatographic column configured as an electrochemical cell. By the incorporation of redox species such as catechols and hydroquinones within the binding sites of the CEs, a new separation process can be envisioned in which the column can be switched between concentration and stripping modes by the electrochemically induced redox transformation of the bound ligand. In addition to the electrochemically induced alterations in binding strengths, the process has the potential for removing target metal ions from HLWs while realizing a reduction in storage volume. This poster presentation will describe the status of these efforts, along with plans and designs of other types of redox transformable extraction phases.

Research Progress and Implications

Progress during the second year of this effort has focused on the design and synthesis of new redox transformable ligands and on procedures for ligand immobilization onto carbonaceous packing materials. Examples include:

1) Achievement of the synthesis of a catechol-containing crown ether ligand which can be electrochemically transformed to its quinone form.
2) Enhancement of the surface coverage of catechol-containing monolayers that are formed via the electrooxidation of amines (e.g., dopamine) by blocking the physisorption of the hydroxyl groups by their metal ion complexation.

Planned Activities

Activities this year target the testing of the recently prepared ligands as well as the synthesis and testing of new ligands. Specific objectives include:

1) Synthesis and testing of metal ion binding capabilities as a function of redox state of crown ether ligands that contain thiol groups that when oxidized to the disulfide form changes the shape and reduces the metal-ion binding ability of the crown ether.
2) Synthesis and testing of metal ion binding capabilities as a function of redox state of catechol-containing ether ligands in which a crown ether-type metal ion binding environment is created when the ligand is attached to an electrically conducting surface. The binding ability of the crown will be dramatically reduced by oxidizing the catechol unit to the quinone form.
3) Synthesis and testing of metal ion binding capabilities of di-hydroxamic acid crown ether ligands that bind to metal ions, e.g. Sr^{2+}, but in the presence of Fe^{3+} form very stable hydroxamic acid complexes in which the geometry of the crown is distorted so as to release the metal ion. In this case, it is the oxidation and reduction of the iron between the +2 and +3 oxidation states that controls the metal ion binding ability of the crown ether.
4) Evaluate the long term stability in alkaline media of coatings formed on carbonaceous materials by the electrooxidation of amines.

Processes Controlling the Migration and Biodegradation of Non-aqueous Phase Liquids (NAPLs) within Fractured Rocks in the Vadose Zone

Karsten Pruess, Lawrence Berkeley National Laboratory

Jennie C. Hunter-Cevera, Lawrence Berkeley National Laboratory

Research Objective

Contamination by non-aqueous phase liquids (NAPLs) in fractured rocks presents a particularly difficult characterization and remediation problem. NAPL migration is likely to be dominated by the highly permeable pathways provided by rock fractures and joints. In arid sites with deep water tables, a significant fraction of near-surface NAPL spills may be contained within the vadose zone. Remediation is impeded by the difficulty to locate the NAPL itself, which through volatilization and dissolution provides a long-term source of wider-spread contamination. Significant inventories

of volatile organic compounds (VOCs) partition and diffuse into less-accessible matrix rock, where removal by flushing or vapor extraction is seriously limited by slow diffusion processes. Biotransformation of these contaminants may remove a significant fraction and contain the spread of contamination.

The objective of this research is to develop a fundamental understanding of the interplay between fluid flow and microbial transformations within the fractured rock vadose zone. This will provide a scientific basis for site evaluation and remedial action for NAPL-contaminated sites. The research is conducted within the context of the geology and contamination at the U.S. Department of Energy's Idaho National Engineering and Environmental Laboratory (INEEL), located in a basalt flow basin where VOC contamination threatens the Snake River Aquifer. However, the results are relevant to other fractured-rock environments.

Our research emphasizes laboratory experiments that examine fluid flow dynamics within the fracture plane and biotransformation processes at the microscale. The mechanistic understanding obtained in these experiments is used to integrate flow dynamics with biological activity in the next generation of experiments in natural rock samples that test the effect of various environmental factors on biotransformations. The biological activity in the integrated experiments is monitored by stable isotope analysis, to support the application of this monitoring technique in the field. Numerical simulation of water seepage in fractures is compared with laboratory observations to extrapolate results to the field scale.

Research Progress and Implications

This report summarizes work after the second year of a three-year project.

We have developed and applied a suite of innovative techniques at the Berkeley Lab's Advanced Light Source to monitor the real-time space-resolved biological activity and chemical transformations on mineral surfaces. These measurements provide a ten-micron spatial resolution of bacterial, mineral and contaminant distribution on the surfaces of geologic media. The techniques include: surface-enhanced infrared reflectance-absorption (SEIR) microspectroscopy with metal-overlayer to monitor the in-situ localization of micro-organisms on mineral surfaces and relate the distribution to the micro-structure and mineral composition of the rocks; SEIR microspectroscopy with metal-underlayer to monitor the microbial responses to environmental stresses, and; synchrotron-based infrared microspectroscopy to nondestructively monitor — in real time — the in-situ transformation of VOCs by microorganisms on natural surfaces of geologic materials. This method also has been used to study metal-organic reactions at the microbe-mineral-contaminant interface.

The application of these techniques has provided mechanistic insights regarding biological activity on mineral surfaces. Using rock-chips from "defensible" core samples from the vadose zone at the Test Area North (TAN) site at INEEL, the relative distributions of contaminant, mineral and microorganisms have been mapped. Microorganisms only occur on vesicle surfaces and not in the matrix rock, and are strongly associated with magnetite minerals, and to a lesser extent with feldspars. Microorganisms were not found on surfaces rich in olivine and pyroxene minerals. The observation that microorganisms associated with magnetite grow the fastest implies that iron-rich rocks have the greatest potential for biotransformation of VOCs. Monitoring the biodegradation of toluene vapor has shown that these techniques allow the identification of unstable intermediate daughter-products that cannot be detected using conventional techniques; this information can be used to identify the rate-limiting steps in degradation pathways. In experiments that investigated the role of relative humidity (RH) on toluene degradation, complete biodegradation occurred at 100% RH, and minimal biomass and degradation occurred at 30% RH. Monitoring of VOC degradation in the presence of mixed-wastes showed that the bacteria reduce some metals to less toxic forms during transformation of VOCs.

Flow visualization experiments of seeping liquids in transparent replicas of natural rock fractures have examined the relationship between the aperture field and flow dynamics for sub-vertical fractures. These experiments have shown that: 1) water flows in narrow channels that spread laterally near asperity contacts and form thin threads as apertures widen, 2) channels flow intermittently even for constant flow or constant pressure boundary conditions, as they undergo cycles of snapping

in the wide aperture regions and subsequent reformation, 3) the frequency of channel snapping increases at higher angles of fracture inclination for a given flow rate and 4) the liquid residence time increases with channel snapping frequency, as indicated by the increased travel time of an electrolyte tracer for higher angles of inclination. Experiments with three fluid phases (NAPL, water, air) show the important role of residual water on enhancing NAPL migration and spreading. Changes in the physical properties of the seeping liquid (density, viscosity, contact angle) have subtle effects on seepage patterns when introduced into an initially dry fracture. A preliminary "rock-replica geocosm" experiment was conducted to visualize water seepage on a natural rock fracture (dense basalt) inoculated with microorganisms. The microorganisms were a mixed culture obtained from the same core sample as used in the micro-scale biotransformation experiments. Over the two-week duration of the experiment, the number of colony forming units in the seepage effluent increased by one order of magnitude, surface tension of the effluent water decreased by 30% and ponding of water due to local clogging of the pore-space affected seepage behavior.

Our theoretical studies of multiphase flow in fractures have emphasized conceptual model development and numerical simulation. Fractures were conceptualized as two-dimensional heterogeneous porous media, and algorithms were developed to synthesize aperture distributions with "realistic" features, including (a) the presence of asperity contacts, where the fracture walls touch, (b) a more or less gradual change towards larger apertures away from the asperities, (c) small-scale fracture wall roughness, and (d) finite-size spatial correlation length among apertures. Numerical simulations of flow in synthetic fractures demonstrated features such as ponding, bypassing, and localization of flow into fast preferential pathways. Sub-horizontal obstacles, such as asperity contacts or fracture terminations, are particularly effective at "funneling" flow into fast preferential pathways. Our results show that seepage in unsaturated heterogeneous media has many features that cannot be understood or approximated in terms of volume-averaged homogenized models. For example, liquid seepage in unsaturated fractures may actually proceed faster in media with lower average permeability. An approximate invariance of seepage under simultaneous space-and-time scaling was theoretically derived. The validity and limitations of this invariance were demonstrated through numerical simulations, and through analyses of capillary- and gravity-driven flows. The scaling behavior suggests that, in fractured media with "sufficiently" high permeability, transient seeps should show a more vertically elongated appearance as the scale of observation increases.

Planned Activities

The developed methods will be used to study the environmental factors that control microbial transformation of VOCs (toluene and TCE) with and without the presence of heavy metals at the micro- and macro-scales. Micro-scale biotransformation experiments will be conducted in micro-bioreactors of basalt rock fragments with cultures obtained from "defensible samples" and exposed to vapor-phase VOCs. Macro-scale biotransformation experiments will be conducted in columns of basalt rock fragments inoculated with the same cultures and exposed to vapor-phase VOC. Comparing the results of macro-scale experiments to the micro-scale should allow an evaluation of mass-transfer limitations to biodegradation, and the efficacy of stable isotope changes to monitor biotransformations.

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Investigation of Groundwater Flow Paths in Fractured Aquifers Through Combined Inversion of Strontium Isotope Ratios and Hydraulic Head Data: The Role of Mixing of Groundwaters From Different Source Areas

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Travis L. McLing, Idaho National Engineering and Environmental Laboratory

Research Objective

Connected zones of high permeability are likely to exist in fractured aquifers, providing fast flow paths that may conduct contamination. Although tracer tests can provide information on local groundwater flow, they do not elucidate regional-scale flow phenomena which is required to understand the long-term evolution of plumes at U.S. Department of Energy (DOE) sites such as the Idaho National Engineering and Environmental Laboratory (INEEL) and Oak Ridge National Laboratory (ORNL). However, natural tracers such as strontium isotope ratios, in conjunction with hydraulic head distributions, can be used to define regional-scale flow behavior. Because the strontium isotope ratio of groundwater evolves over time towards that of the aquifer host rock, strontium isotopes can be used to define groundwater flow paths. In the absence of mixing of waters from different sources, strontium isotope ratio contours will be roughly orthogonal to groundwater flow paths. In aquifers such as the Snake River Plain Aquifer (SRPA) in which the mixing of waters from different sources is important, the use of conservative constituents and isotopic ratios as well as inverse modeling of water mixing can be used to delineate the relative contributions of water-rock interactions and mixing. Through the use of state-of-the-art inversion techniques, both hydraulic and chemical data can be used to define regional flow paths and identify large-scale subsurface features controlling connected zones of high permeability. This project is part of a multi-institutional (T. Johnson, Univ. of Illinois and C. Doughty, Lawrence Berkeley National Laboratory) investigation of fast flow paths within the SRPA with overall objectives as described above. Specific objectives for this project include (1) elucidating the role of mixing water from different recharge sources on groundwater composition, (2) defining the relative hydrochemical contributions of aquifer basalt flows and sedimentary interbeds to groundwater composition, and (c) determining the scale at which water-rock interactions become more important than mixing.

Research Progress and Implications

This report summarizes the accomplishments through the first 24 months of the 30-month performance period. During this time, the investigators, in collaboration with the U.S. Geological Survey, collected groundwater samples from numerous wells located across the SRPA and made field measurements of pH, alkalinity, conductivity, and dissolved solids. Water samples were provided to our project collaborators for chemical and isotopic analyses. The isotopic data define regions of high and low $^{87/86}$Sr ratios at the INEEL. At the toes of the Lost River and Lemhi mountains on the northwest boundary of the INEEL are two regions of anonymously low $^{87/86}$Sr ratios. These regions of low $^{87/86}$Sr ratios represent zones of slower groundwater flow and are adjacent to fast flow zones aligned parallel to the drainage basins of these mountains. Suggesting that groundwater moves much slower at the toes of the Lost River and Lemhi mountains than in the rest of the aquifer. Because of the slower flow, thermal water up-welling from deep in the aquifer (at depths greater than 300 meters) carries more equilibrated water into the effective portion of the aquifer leading to a lighter isotopic signature of the groundwater in these slow flow regions. In addition to thermal up-welling, water in slower flow zones are in contact with the basalt matrix for longer periods of time, resulting in minor hydration of intersertial basalt glasses. The coupling of these two processes provides an explain for the differences in $^{87/86}$Sr ratios. The identification of diagenetic phases in well cores collected from the base of the effective portion of the aquifer and the discovery of a significant population of methanotrophs in the groundwater support the existence of geothermal water up-welling into the more conductive portion of the SRPA. In addition, the complete absence of geothermal springs on the recently volcanically active Snake River Plain (SRP) and the large number of hot springs located on the periphery of the plain strongly suggest the presence of a significant geothermal source for the SRPA. The results of earlier models generated to characterize the flux of geothermal water to the aquifer were based on water chemistry from a hot spring located on the northeast border of the plain. These models indicated that less than 1% of the solute budget of the SRPA results from of geothermal up-welling. Because few wells penetrate into the deeper portion of the SRPA it is difficult to test the hypothesis that thermal water is up-welling into the effective portion of the aquifer. A 1,000-meter rhyolite-hosted thermal well near Ashton, Idaho and a 3,400-meter thermal well at the INEEL were sampled to determine the water chemistry for deep thermal water under the SRP. The $^{87/86}$Sr ratio at the two wells is close to that of the host rock. Current models based on these new data indicate that a much larger amount of geothermal water up-wells into the aquifer than was previously believed.

Planned Activities

Modeling and research activities will conclude during the summer of 1998. A paper will be submitted to a journal in the fall of 1998 detailing the results of the research.

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