Mixed Waste

New Anion-Exchange Resins for Improved Separations of Nuclear Materials

Project ID: 54770

Dr. Mary E. Barr, Los Alamos National Laboratory

Dr. Richard A. Bartsch, Texas Tech University
Dr. Gordon D. Jarvinen, Los Alamos National Laboratory

Research Objective

We are developing bifunctional anion-exchange resins that facilitate anion uptake by carefully controlling the structure of the anion receptor site. Our new ion-exchange resins interface the rapidly developing field of ion-specific chelating ligands with robust, commercial ion-exchange technology. 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. Resin materials that 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 (PVP) with a second cationic site, such that the two anion-exchange sites are linked by 'spacer' arms of varying length and flexibility.

The overall objective of our research is to develop a predictive capability that allows the facile design and implementation of multi-functionalized anion-exchange materials to selectively sorb metal complexes of interest from targeted process, waste, and environmental streams. Various *Focus Areas and Crosscutting Programs* have described needs that would be favorably impacted by the new materials:*Tanks*, *Plutonium*; *Subsurface Contaminants*; *Mixed Waste*; and *Efficient Separations*. Sites within the DOE complex which would benefit from the improved anion-exchange technology include Hanford, Idaho, Los Alamos, Oak Ridge, and Savannah River.

Research Progress and Implications

As of March 2000, this report summarizes work near the end of our highly successful 3-year project. Our technical approach has combined 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 interactions at the metal complex/functional-site. *Synthesis and evaluation* of bifunctionalized extractants and ion-exchange materials that implement key features of the optimized binding site provide feedback to the *modeling and design activities*.

Actinide-complex speciation: The primary actinides of interest in nitrate solutions have been plutonium (IV) and americium (III). We have refined plutonium mono- and di-nitrato formation complexes. We find that addition of water-soluble anion-exchange polymers to solutions of plutonium in nitric acid shifts the solution equilibrium to favor the dianionic hexanitrato complex, but with K_d values orders of magnitude lower than for sorption onto solid resins. Even Am(III), which does not form anionic nitrato complexes in pure nitric acid media, binds to the anion-exchange resins in solutions with excess nitrate. We are awaiting EXAFS data analysis (on Nd(III) surrogates) to determine the exact anionic species in solution and sorbed to the resin. We have conducted promising 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 systematic series of bifunctional resins that examine 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 both americium and plutonium uptake from nitrate solutions. Soluble polymers based on linear PVP display similar trends.
3) The percent crosslinking of the substrate: Decreasing the crosslinking from 25% to 18% yields an *ca.* 50-100% increase in K_d 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%.

We synthesized and evaluated a tri-functional (polystyrene-based) resin for plutonium and americium uptake. Despite the higher cationic charge density, it did not display enhanced Am(III) uptake. We have completed the synthesis, but not the evaluation, of bifunctional extractants. We were able to achieve the desired 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 successfully demonstrated that our simple molecular mechanics-based model is sufficient to predict which 'spacer' length is optimal for electrostatic binding of the Pu-hexanitrato dianion with the dicationic 'resin site' (modeled as a free pyridinium species). Thus, we have established that even diffuse and non-directional ionic bonding interactions are determined by many of the same forces as strong, directional covalent interactions (*i.e.,* the 'chelate' effect on entropy, optimized 'bite' size, *etc.*) We have also confirmed our molecular-mechanics models with *ab initio* calculations and have used these calculations to help determine the overall enthalpic and entropic contributions to the ΔG of sorption from solution onto the solid exchangers. Correlation with experimental data is good using both formal charge and partial charge models. Models show that a 1,4-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, leading to the hypothesis that a 1,4-*cis*-2-butene spacer may exhibit improved sorption kinetics. This hypothesis was supported by experimental results, although the effect was not as significant as we had hoped. Subsequent modeling of diffusion properties show that bulk diffusion rates of solution into the solid matrix are rate-determining. Studies using analogous soluble polymers, based on linear PVP, are not complicated by diffusion or phase-change energy terms, and thus provide clear support for the assumption in our model that these terms are essentially constant for a given series of resins.

Future Work and Application

These new anion-exchange materials are still being evaluated for use at LANL for plutonium process improvement, ^{238}Pu recovery and Am removal from pre-cementation wastes. We hope to capitalize on our licensing agreement with Reilly Industries to continue development of this new class of resins for large-scale commercial applications, as well as for select EM needs.

Patent and Licensing Agreement

US Patent #5,670,550 (Sept. 23, 1997) - "Ion-Exchange Polymers for Anion Separations"
Materials and applications licensing agreement - Reilly Industries, Indianapolis, Indiana - May 1999.

Publications and Presentations

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment" Marsh, SF; Jarvinen, GD; Bartsch, RA; *Reactive Polymers* **1997**, *35*, 75-80.

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment" Marsh, SF; Jarvinen, GD; Bartsch, RA; Nam, J.; Barr, ME; *J. Radioanal. Nucl. Chem.* , **1998**, *235*, 37-40.

"Development of Anion-Exchange Resins for Separations of Actinides" Barr, ME; Jarvinen, GD; Marsh, SF; Bartsch, RA, Abstracts ACS, v. 213(pt. 2) p. 73-IEC Apr. 13, **1997**.

"Sorption of Pu(IV) by Soluble Anion-Exchange Polymers" Barr, ME; Jarvinen, GD, Moody EW, Vaughn, RB; Abstracts ACS,v.216(pt.2) pp. 88-NUCL AUG 23, **1998**, and v.216(pt.1) pp. 5-TECH AUG 23, **1998**.

"Americium Separations from Complex Mixtures using Anion Exchange" Barr ME, Jarvinen GD, Schulte LD, Stark PC, Chamberlin, RM; Abstracts ACS, v. 217 pp. 019-IEC MAR 21, **1999**.

"Sorption of Pu(IV) from Nitric Acid by Bifunctional Anion-Exchange Resins" Bartsch, RA, Zhang ZY, Elshani S, Zhao W, Jarvinen GD, Barr ME, Marsh SF, Chamberlin RM; Abstracts ACS, v. 217 pp. 125-IEC MAR 21, **1999**.

"QSAR of distribution coefficients for actinide hexanitrato complexes" Moody EW, Barr ME, Jarvinen GD; Abstracts ACS, v. 217(pt.2) pp. 170-NUCL MAR 21, **1999**.

Managing-Tight Binding Receptors for New Separations Technologies

Project ID: 54791

Daryl H. Busch, University of Kansas

Richard S. Givens, University of Kansas

Research Objective

This program is directed at establishing the fundamental principles that will make the most strongly binding ligands and their complexes available to separations technologies.The ultimate powerful ligands can capture metal ions in the most competitive of circumstances. Ultra tight-binding ligands can remove metal ions from mineralized sites, take them away from lesser ligands, and even capture metal ions from extremely dilute solutions. Further, these feats offer the possibility of solving some of the most serious environmental challenges that cannot be met by existing techologies: decontamination of metal surfaces, removal of metal contaminations from soils, separation of very low concentrations of radioactive metal ions from nuclear waste, capturing of contaminating metal ions from extremely dilute solutions. Despite their promise, extremely stable complexes are rarely used in separations because their great stabilities are accompanied by very slow rates of complex formation and dissociation. Specifically, this program has attacked this limitation in two ways: (1) seeking basic scientific ways of overcoming the natural molecular lethargy of ultra tight-binding ligands and (2) developing a new technology that functions despite the slowness of the metal binding reactions. The three basic concept areas of this program are: replace slow equilibrium formation and dissociation of ultra tight-binding complexes by (1) *switch-binding of templating ligands, and* (2) *switch-release* of photo reactive ligands, and (3) create a slow separations technology based on imprinted polymers (e.g., a soil poultice)

Research Progress and Implications

(1) Switch-binding of templating ligands. Figure 1 shows our Generation 1 switch-binding ligand and the template ring closing. Both the synthesis and quantitative characterization of the new family of ligands were challenging because the target molecule, by design, reacts with itself. These problems were overcome and template ring closure upon contacting nickel(II) in aqueous solutions was proven by isolation of the macrocyclic nickel complex (isolated yield, 82%), and solution studies. Kinetic studies on the acid destruction of the complex showed the stabilization expected for a

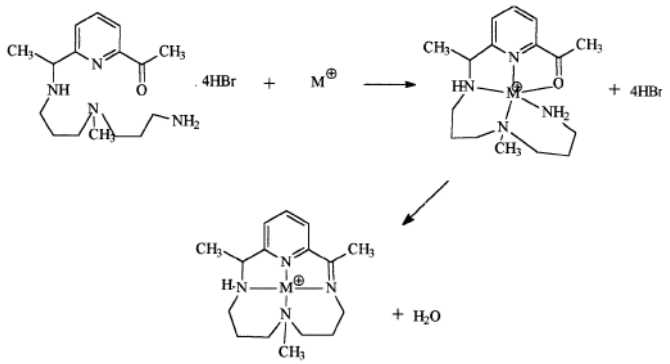


Figure 1

macrocyclic complex. As expected, two rate processes occur during switch-binding to nickel(II); rapid "first complexation" on the millisecond time scale, followed by a slower process in which the chelation process is completed. Our preliminary analysis gives the rate constant for the critical final macrocyclization step $k_2 = 6.05(\pm 0.48)x10^{-2}s^{-1}$. A very similar linear ligand that cannot cyclize gave $k_2 = 3.07(\pm 0.21)x10^{-2}s^{-1}$. Equally important, comparison of the rate constants for our switch-binding reaction with those for complex formation using similar macrocycles shows that the new ligands bind more rapidly by a factor of two or three orders of magnitude. The result suggests that switch-binding macrocycle formation may be as fast or faster than ordinary chelation.These studies have already provided a proof of concept for the switch-binding principle. A second generation of switch-binding ligands has been designed and synthesized in which the ring closing reaction is amide or ester formation.

(2) Switch-release of the Metal Ion. The synthesis of an o-nitrobenzyl substituted cryptand **(Figure 2)** has been achieved, in an overall yield of 38%, by modifications of a known reaction sequence and the preliminary photochemistry examined. Upon photolysis, the cryptand was converted to the open macrocycle in quantitative yield following the typical photochemical sequence of *o*-nitrobenzyl derivatives. Further studies will determine the photo efficiency for this transformation, the effects of different metal ions on the nature of the reaction products and on the dissociation constants. Recyclization of the photolyzed product back to the cryptand by sequential oxidation of the nitroso group, reduction of the carbonyl and cyclization is under study.

(3) A Soil Poultice based on Imprinted Macroporous Polymers. This proposed new slow-binding technology mimics the manner in which certain microbes bring iron into their cells from minerals in the soil. An extremely tight-binding ligand is excreted through the cell membrane of the microorganism; it diffuses into the soil and slowly dissolves iron from the abundant oxide. The complex then diffuses back into the cell. To mimic these natural systems our "soil poultice" makes use of youthful materials called "templated macroporous polymers"which contain highly selective receptors. Casting the polymer in the presence of their target molecules locks in a structure favoring their binding. In this system, a solution of the selected ligand is sprayed on the contaminated soil, the ligand extracts the contaminant and polymer beads selectively adsorb the metal/ligand complex, thereby removing the insoluble contaminant from the soil. The active monomer was acrylamide, highly crosslinked with ethylene glycol dimethacrylate to produce polymers with mesopores (20-500Å diameter). Amide groups are known to favor rebinding to templated polymers so the favored target complex had the ligand of **structure 1**.The mode of interaction is shown in **Figure 3**. The new

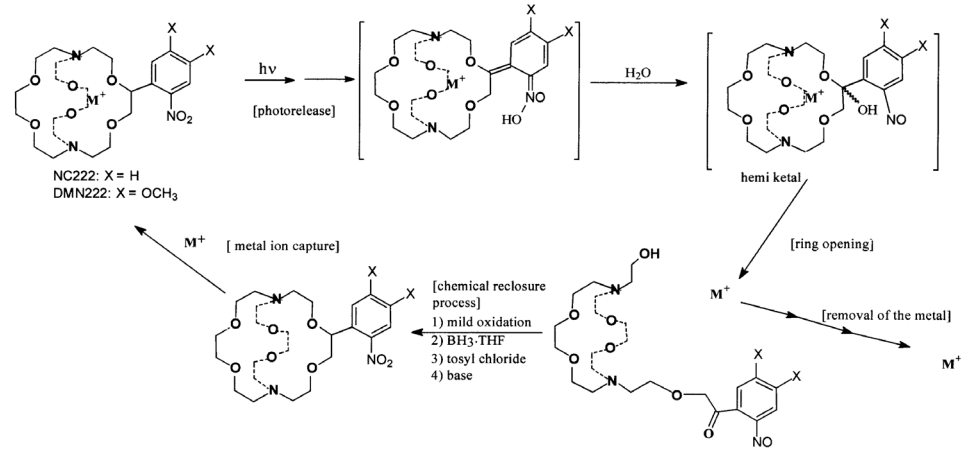
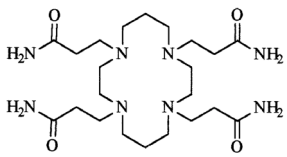


Figure 2



Structure 1

polymers were characterized by infrared spectroscopy, polymer swelling, and surface area/porosity measurements. For samples of good porosity, rebinding equaled the best expected results for selective hydrogen-binding sites. Extremely promising results were obtained when a counter ion was also included in the polymer.

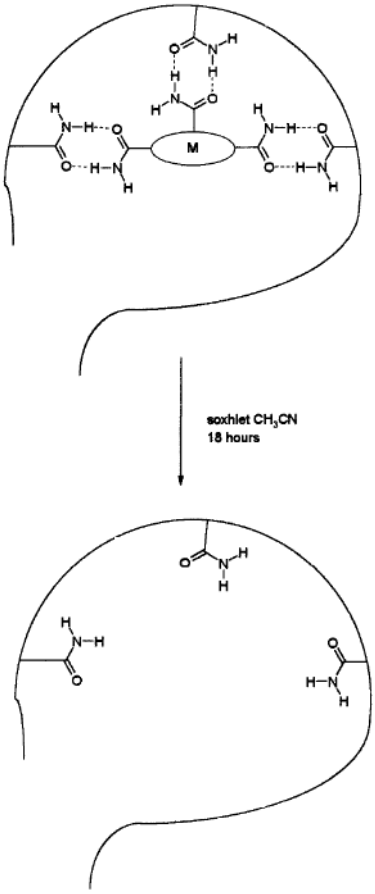


Figure 3

Utilization of Kinetic Isotope Effects for the Concentration of Tritium

Project ID: 55103

Gilbert M. Brown, Oak Ridge National Laboratory

Thomas J. Meyer, The University of North Carolina at Chapel Hill
C.-H. Ho, Oak Ridge National Laboratory
Leon Maya, Oak Ridge National Laboratory
Bruce A. Moyer, Oak Ridge National Laboratory
Frederick V. Sloop, Jr., Oak Ridge National Laboratory

Research Objective

Tritium in groundwater is in the form of HTO which exchanges rapidly with normal isotopic composition water making it highly mobile. There is no currently identified, cost effective technology that is a solution to the problem of low level tritium contamination at a number of DOE sites. The most serious problems are at the Savannah River Site (SR00-3016 and SR004014) and the Hanford Site (RL-MW023) although a significant concern was identified at LLNL (OK99-13). The objective of our work is to develop an electrochemically based method to remove tritium from contaminated water, and as a consequence of the process tritium will be incorporated into an organic compound that will not readily exchange the tritium with groundwater.

Research Progress and Implications

Work is in progress 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. The process will 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 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.

Progress has been made toward demonstrating the individual steps required for the concentration of tritium in water in the three years and 4 months of this project. An early research objective was achieved to demonstrate the individual steps for a proof-of-principle "cold" experiment to separate deuterium from water in a cyclic process. The electrochemical reduction of carbon dioxide in an aqueous solution containing deuterium shows the incorporation of deuterium in the formate anion product. In a cyclic process, reduction of CO_2 will be coupled to the Ru(IV) catalyzed oxidation of the formate anion. We demonstrated the fractionation of the deuterated component in a mixture of proteo- and deutero-formate. The Ru(IV) oxo species chosen for this work was the complex $[Ru(IV)(terpy)(bpy)O]^{2+}$ where terpy is 2,2´,2´´-terpyridine and bpy is 2,2´-bipyridine. We have determined the tritium kinetic isotope effect (k_H/k_T) for oxidation of formate by the complex $[Ru(IV)(terpy)(bpy)O]^{2+}$. Measurement of the kinetic isotope effect for oxidation of tritiated formate anion was made at the tracer level by measuring the rate of transfer of tritium from the formate anion to water. The tritium kinetic isotope effect, k(H)/k(T), is dependent on ionic strength, and at μ 0.1 M

it was observed to be in excess of 300. This result has both scientific and technological significance. It is the largest kinetic isotope effect observed at ambient temperatures, and it demonstrates the importance of nuclear tunneling in the hydride transfer mechanism. The technological significance is that tritium and protium can be separated in a single stage. In terms of more long-range goals, progress has been made in additional areas. We have begun to develop the catalytic chemistry in redox active films and membranes on the electrode surface, configurations that might be appropriate for device applications. The second general theme is to evaluate C-H/C-T kinetic isotope effects in the oxidation of several functionally different organic substrates by Ru(IV) oxo complexes. An investigation of the chemistry of related high oxidation osmium terpyridyl complexes has been rewarding. Oxo-like reactivity was observed for high oxidation state osmium hydrazido complexes. The proton–coupled electron transfer reaction of an osmium hydrazido complex was observed to have a N-H/N-D kinetic isotope effect of 41.4. These reactions may have significance for devising more effective catalyst-organic substrate combinations.

Planned Activities

As time and funding levels permit, the tritium isotope effect for oxidation of a derivative of benzyl alcohol by $[Ru(IV)(terpy)(bpy)O]^{2+}$ will be determined. Conditions will be investigated for reduction of the benzyl alcohol derivative by H_2 at low pressures.

Information Access

Oxo-Like Reactivity of High Oxidation State Osmium Hydrazido Complexes. Huynh, M. H. V.; El-Samanody, E.; Demadis, K. D.; Meyer, T. J.; White, P.S. J. Am. Chem. Soc., **1999**, *121*, 1403-1404.

Mechanisms of Surface Electron Transfer. Proton-Coupled Electron Transfer. Trammell, S. A.; Wimbish, J. C.; Odobel, F.; Gallagher, L. A.; Narula, P. M.; Meyer, T. J. J. Am. Chem. Soc. **1998**, *120*, 13248-13249.

The Effect of Stepwise Oxidation on Molecular Structure in Osmium Hydrazido Complexes. Huynh, M. H. V.; El-Samonody, E-S.; Meyer, T. J.; White, P. S., Inorg Chem., **1999**, *38*, 3760.

Proton-Coupled Electron Transfer from Nitrogen. A N-H/N-D Kinetic Isotope Effect of 41.4". Huynh, M. H. V.; White, P. S.; Meyer, T. J. J Amer Chem Soc., **1999**, *121*, 4530-4531.

Intramolecular Oxidative Substitution on Coordinated Terpyridyl Ligand. Huynh, M. H. V.; Lee, D. G.; Meyer, T. J.; White, P. S., J Amer Chem Soc., **1999**, *121*, 10446-10447.

Surface Catalysis of Solution Electron Transfer. Narula;P. M.; Trammell, S. A.; Meyer, T. J., in preparation.

Reduction of Benzoquinone by trans-[OsIV(tpy)(Cl)2(N(H)N(CH2)4O)](PF6). Proton-Coupled Electron Transfer from Nitrogen. Huynh, M. H. V,. Meyer, T. J., in preparation.

H/D Isotope Separation based on Kinetic Isotope Effects, P. M. Narula, F. V. Sloop, G. M. Brown, L Maya, and T. J. Meyer, in preparation.

Deuterium and Tritium Kinetic Isotope Effects for the Oxidation of Formate by (Terpyridine)(bipyridine)-(oxo)ruthenium(IV), G. M. Brown, F. V. Sloop,Jr., B. A. Moyer, and T. J. Meyer, in preparation.

Photocatalytic and Chemical Oxidation of Organic Compounds in Supercritical Carbon Dioxide

Project ID: 54847

Dr. Daniel M. Blake, National Renewable Energy Laboratory

Research Objectives

The objectives are 1) 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) Explore the use of supercritical carbon dioxide as a solvent for the photocatalytic oxidation of organic compounds and 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 annual report covers progress during the second year of the project, ending in May 1999. During the first year a system was designed, constructed, and modified so that the photocatalytic oxidation of organic compounds could be carried out in supercritical carbon dioxide. Prior to this work there were no reports of photocatalytic oxidation using titanium dioxide catalysts in supercritical fluids. The experimental system is now being operated at temperatures from 25-50 C, pressures from 15-5000 psi, and with gas, liquid, and supercritical fluid phases. The concentration of organic solutes can be followed using on-line gas chromatography and UV-Vis spectroscopy. Experiments during the past year measured the rates of oxidation of benzene, toluene, hexane, cyclohexane, and acetone in gas phase (80:20 N_2:O_2 or CO_2:O_2) and in supercritical CO_2 ($SCCO_2$). Rates are lower in supercritical CO_2 than in the gas phases. This may be due to reduced diffusion rates in the supercritical phase, competitive CO_2 adsorption, or differences in flow rates in the supercritical phase experiments.

This report summarizes work done during the first two years of the project. There have been more than 3000 publications on photocatalytic chemistry of titanium dioxide for removal of organic and inorganic compounds from water and air or partial oxidation of organic compounds in air or organic solvents but no work has been reported in supercritical fluids.[1] The work reported here has demonstrated for the first time that photocatalytic chemistry can also be carried out in supercritical carbon dioxide. We have also compared the reaction in air and gas phase carbon dioxide with that in supercritical CO_2. The results we have obtained on the photocatalytic oxidation of selected organic compounds in gas and supercritical phases must be considered preliminary since we are still working on achieving well-defined flow and light exposure conditions in the experimental system. Never the less, the results establish that representative classes of organic compounds can be reduced from about 2000 ppmv to below detection in supercritical carbon dioxide by photocatalytic oxidation. A preliminary communication is being prepared.[2]

A schematic diagram of the experimental system for carrying out the experiments is shown in Figure 1. During an experiment the fluid phase is recirculated within the part of the system closed in

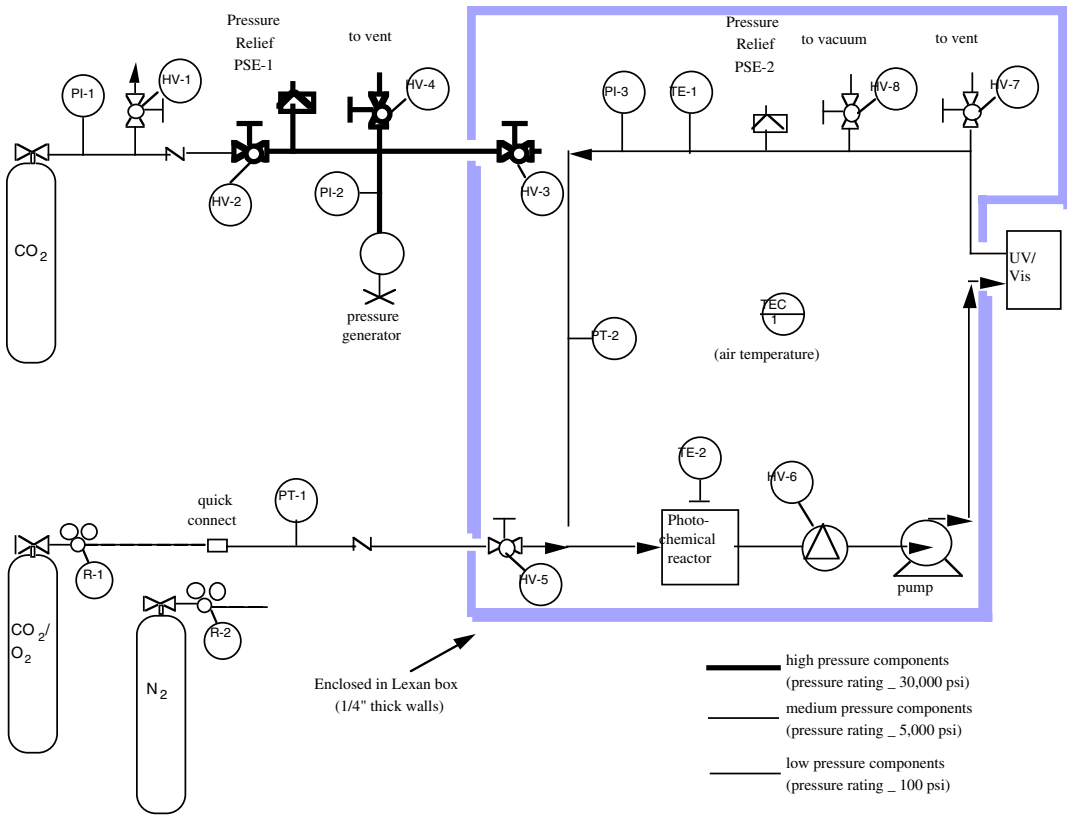


Figure 1. Schematic diagram of the experimental system.

the Lexan box and through the view cell and the sampling valve of the gas chromatograph, co-located with the UV-Visible spectrometer.

Representative reaction conditions are: initial concentration of the organic compound is approximately 2000 ppm; initial concentration of O_2 > 50 times stoichiometric amount; the photocatalyst is Degussa P25 TiO_2 on 5mm glass beads; gas phase experiments were performed at ~10 psig and 25 C; supercritical phase experiments were performed at ~1200 psig; T~37 C; and the reaction vessel was illuminated with a 100 watt spot lamp with output centered at 360 nm.

Results are shown in Figures 2 through 5. The results for hexane, toluene, cyclohexane, acetone and benzene oxidation in synthetic air are shown in Figure 2. The rate of oxidation of benzene is typically lower than other hydrocarbons. There is evidence that intermediate oxidation products (e.g. phenol, catechols, and quinones) are strongly adsorbed on titanium dioxide and the rate is determined by the time required to oxidize these intermediate products and create free sites for benzene.[3] Comparison of the oxidation of the same compounds in a carbon dioxide/oxygen mixture yielded similar results as is shown in Figure 3. Carbon dioxide had little effect on the rates in the gas phase reaction.

Figure 4 shows that the rate of oxidation of hexane is moderately lower in supercritical CO_2 compared to the gas phase. For benzene, Figure 5, there is little difference between the gas and supercritical phases. As mentioned above, the photocatalytic oxidation of benzene and other aromatic compounds is limited by the rate of oxidation of adsorbed, intermediate oxidation products to free surface sites. Supercritical CO_2 is apparently not sufficiently polar to dissolve the intermediate oxidation products and keep the surface open for benzene oxidation.

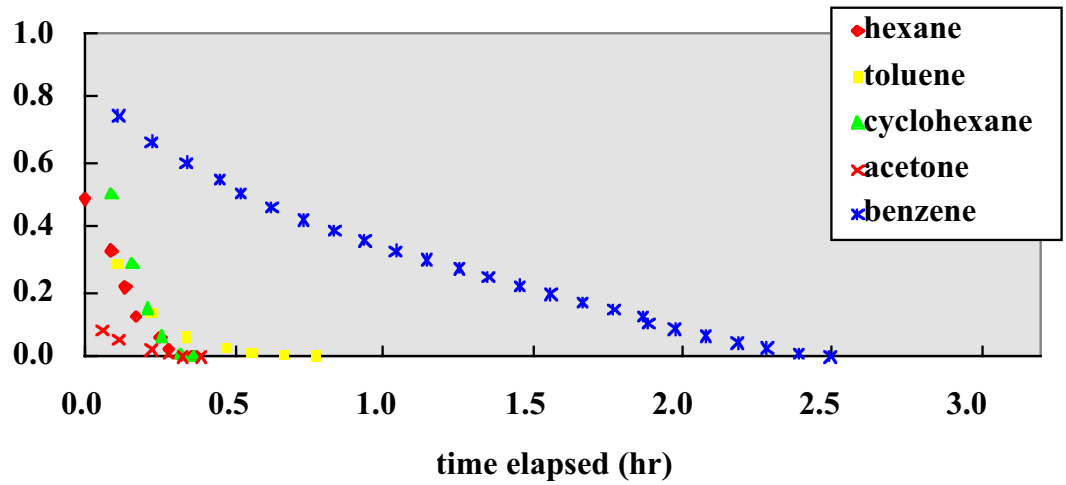


Figure 2. Oxidation of Organics in N_2/O_2 (80:20)

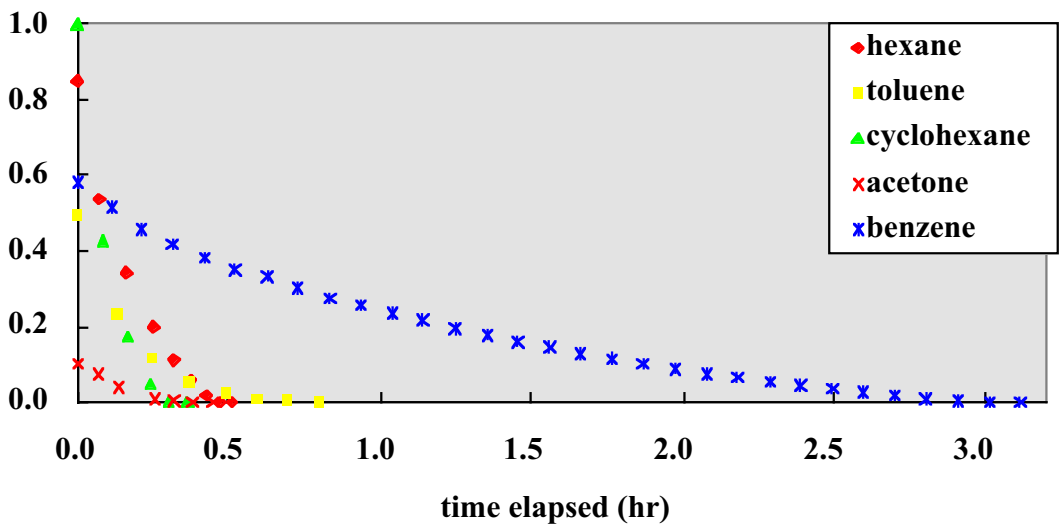


Figure 3. Oxidation of Organics in Gas Phase CO_2/O_2 (80:20).

Planned Activities

Work to date has established that photocatalytic oxidation of organic compounds can be used to purify supercritical carbon dioxide. This establishes the technical feasibility of the proposed approach. During the final year of the project effort will be directed toward obtaining quantitative data that can be used to better define the process for representative organic compounds. Further contacts will be made with others in the DOE complex that are pursuing applications for cleaning materials or parts with supercritical carbon dioxide.

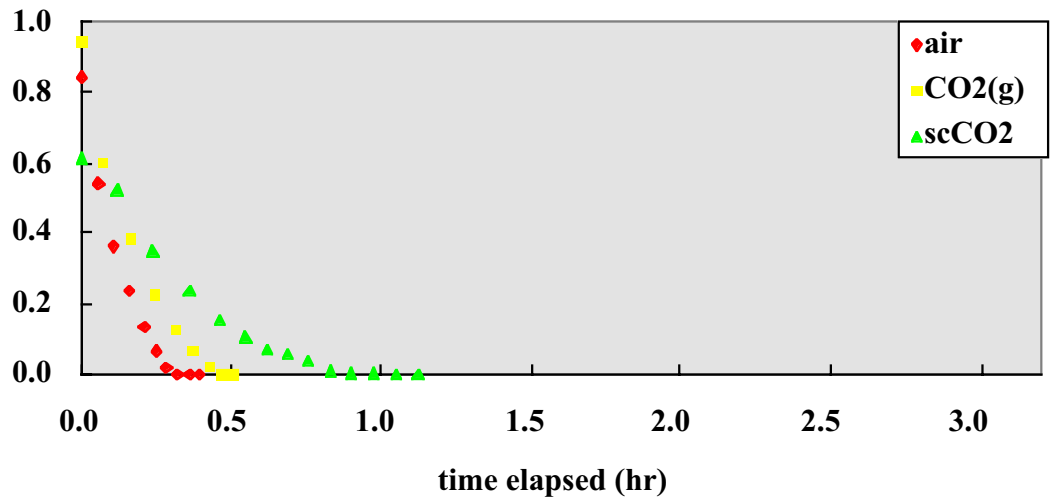


Figure 4. Hexane Oxidation in Gas Phase N_2/O_2 or CO_2/O_2 and in Supercritical CO_2/O_2

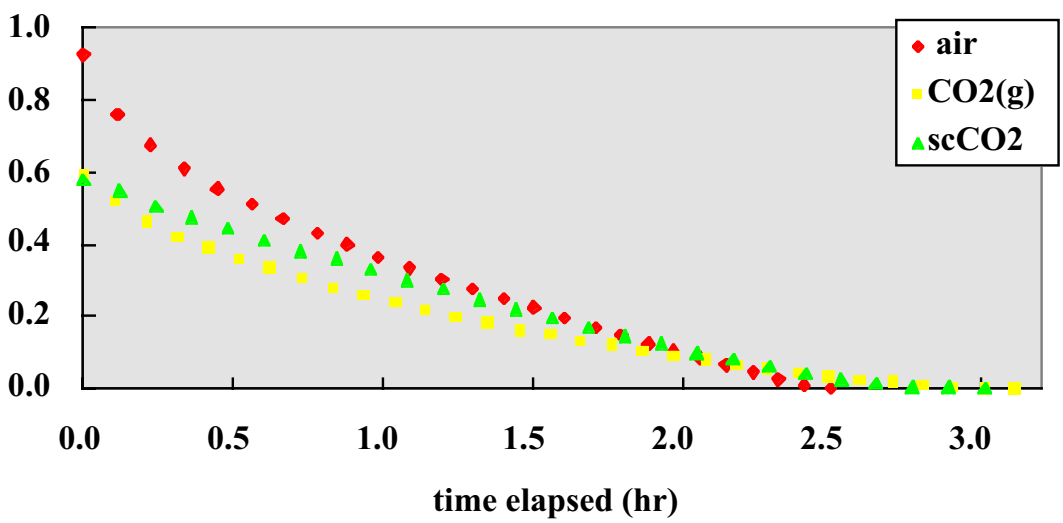


Figure 5. Benzene Oxidation in N_2/O_2, Gas Phase CO_2/O_2 and Supercritical CO_2/O_2

References

1 (a) Blake, Daniel M. (1994). *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air*. NREL/TP-430-6084. Golden, CO: National Renewable Energy Laboratory. 75 pp. [DE94006906] Available from the National Technical Information Service, Springfield, VA 22161. (b) Blake, Daniel M. (1995). *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air. Update Number 1, to June, 1995*. NREL/TP-473-20300. Golden, CO: National Renewable Energy Laboratory. 102 pp. Available from the National Technical Information Service, Springfield, VA 22161. (c) Blake, Daniel M. (1997). *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air. Update Number 2, to October, 1996*. NREL/TP-430-22197. Golden, CO: National Renewable Energy Laboratory. 88 pp. Available from the National Technical Information Service, Springfield, VA 22161. (d) Blake, Daniel M. (1999). *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air. Update Number3, to January, 1999*. Golden, CO: National Renewable Energy Laboratory. In Preparation.

2 Debra L. Bryant, Daniel M. Blake, and Edward J. Wolfrum. Manuscript in Preparation (1999).

3 Jacoby, William A., Daniel M. Blake, John A. Fennell, James E. Boulter, LeAnn M. Vargo, Marya C. George, and Suzanne K. Dolberg. "Heterogeneous Photocatalysis for Control of Volatile Organic Compounds in Indoor Air." *J. Air Waste Manage. Assoc.,* 46, no. 9 (1996): 891-8.

De Novo Design of Ligands for Metal Separation

Project ID: 55223

Dr. Garland R. Marshall, Washington University

Research Objective

This application focuses on the development of appropriate computation tools and parameters for the de novo design of selective metal ligands.

Research Progress and Implications

We have developed a successful suite of tools for computer-aided design of ligands for receptors of known three-dimensional structure (structure-based design), including the prediction of affinity. Adaptation of the algorithms to place donor atoms at appropriate geometrical locations surrounding the metal of interest, rather than filling up a cavity with donor/acceptor atoms placed optimally to interact with a protein active site, is straightforward. Appropriate geometrical parameters for metals can be derived from crystal structures and force constants adapted from recent advances in theories of metal-ligand interactions. The practical goal is computer-aided design of ligands which would be selective for one metal over another with a predicted selectivity ratio and affinity.

Rational Synthesis of Imprinted Organofunctional Sol-Gel Materials for Toxic Metal Separation

Project ID: 60096

Ziling (Ben) Xue, University of Tennessee Knoxville

Craig E. Barnes, University of Tennessee Knoxville
Sheng Dai, Oak Ridge National Laboratory

Research Objective

The objective of this program is to rationally design and synthesize imprinted sol-gel SiO_2 and SiO_2-MO_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 tailored hybrid inorganic-organic materials. These hydrophilic 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 recognition and binding of target RCRA metal ions.

Research Progress and Implications

As of February 2000, the research progress in five months (9/15/99 - 2/15/00) of this three-year project is summarized here. We have successfully prepared sol-gels grafted or doped with organic ligands specific for binding targeted RCRA metal ions Cu^{2+}, Hg^{2+}, UO_2^{2+}, Sr^{2+}, and Cs^+. When these organofunctional sol-gels are exposed to solutions containing the targets, they quickly remove them from aqueous solutions. In many such sol-gels, the metal ions absorbed in the sol-gels can be easily removed to regenerate the organofunctional sol-gels for subsequent cycles of metal ion removal. Work during this period has focused on the following areas: (1) Study of the critical factors necessary for the efficient preparation of highly selective imprint mesoporous sol-gels; (2) Developing new ligand as well as grafting and doping procedures for producing mesoporous hybrid sol-gel materials with anchored ligands; and (3) Investigations of bimetallic (Ti/Si) oxide systems for the removal of Cs^+ and UO_2^{2+} ions from aqueous solution.

(1) Imprinting Design and Methodolgy for Sol-Gels. We have conducted an extensive series of investigations to elucidate the critical factors involved in the efficient preparation of imprinted, hybrid sol-gel based sorbents designed to selective remove target RCRA metal ions. Three different procedures are currently under investigation which can be considered first, second and third generation imprinting procedures. First generation imprinting involves anchoring a templated collection of ligands around a target [Cu^{2+}, Hg^{2+}, Cs^+, UO_2^{2+} (depleted)] on a preformed silica surface. Preliminary studies using diamine reagents for the selective binding of Cu^{2+} ions gave rise to relative selective coefficients k' [$k' = k_{\text{imprint-coated}}/k_{\text{control}}$; $k = K_{\text{d (target)}}/K_{\text{d (Zn competitor)}}$] as large as 40 which, to our knowledge, are the largest values currently reported for imprinted metal ion sorbents. Second generation imprinting studies involve anchoring the ligand-target template onto the pore surfaces of "as synthesized" mesoporous sol-gels via ion exchange equilibria between the charged template aggregate and surfactant molecules used to develop mesoporosity. This procedure bypasses the need to remove the surfactant in a separate step and preconditioning of the support surface for grafting ligand-target templates. Preliminary studies with amine-copper templates have lead to high surface area sorbents effectively functionalized with higher ligand loadings than attainable by conventional coating procedures. Third generation imprinting (as known as hierarchical double-imprinting) involves combining and controlling the adsorption process (imprint formation) and pore structure forming reactions simultaneously. Thus, while surfactant based micelles enforce mesoporosity (>20 Å diameters) on

the forming gel, target ion-template complexes graft into these surfaces to produce, once the metal is removed, templated cavities which are ordered on the molecular level (1-3 Å). Preliminary studies with copper-amine templates have produced very selective sorbents with relative selectivity coefficients k′ (> 200).

(2) Direct Sol-Gel Approaches to Anchored and Doped Ligands for the Removal of Sr^{2+}, Cu^{2+} and Hg^{2+}. A substituted diaza-18-crown-6 with high affinity for Sr^{2+} has been encapsulated in sol-gels by a simple, one-step approach. The Sr^{2+} uptake studies determined the doped gels absorbed Sr^{2+} quickly with both high capacity and selectivity in the presence of excess Ca^{2+}. The loaded gels could be efficiently stripped of Sr^{2+} with a single acid wash and, after neutralization, cycled for repeated Sr^{2+} binding without loss of performance.

Commercially available ethylenediamine ligands linked to $-Si(OR)_3$ groups have been used to adsorb both Cu^{2+} and Hg^{2+} ions from aqueous solution. The gels are prepared by mixing the anchored diamine ligands with $Si(OMe)_4$ in water. Cu^{2+} uptake and release (under acidic conditions) were studied through several cycles. No loss of binding affinity was observed. Selectivity studies between Cu^{2+}, Zn^{2+} and Cd^{2+} showed that the grafted amine ligands bound Cu^{2+} ions in preference to either competitor.

(3) Bimetallic (Ti/Si) Oxide Systems for the Removal of Cs^+ and UO_2^{2+}. Microporous metal oxides readily adsorb uranyl ions via ion exchange reactions with surface silanols. Little is known about the adsorption properties of mesoporous analogues of these oxides. We have prepared a series of mesoporous mixed SiO_2-TiO_2 (100→0% Si vs. Ti) and studied the binding affinity exhibited toward uranyl ion. Kinetic studies conclusively showed that uranyl uptake by mesoporous sorbents is much faster than with comparable microporous materials while total surface decreased with increasing titanium content. This result is consistent with uranyl binding primarily to TiO_2 sites on the surface.

Both coated and homogeneous mixed mesoporous SiO_2-TiO_2 have been prepared and their affinity for Cs^+ studied. Coated materials were prepared by exposing precalcined mesoporous silica to titanium isopropoxide $Ti(OPr^i)_4$ and water while homogeneous mesoporous (d_{ave} = 44 Å) SiO_2-TiO_2 were prepared by mixing $Si(OMe)_4$, $Ti(OPr^i)_4$, water and the neutral block copolymer Tergitol 15-s-15 surfactant together. At pH >10 both coated and homogeneous Si-Ti sorbents removed >90% of the Cs^+ from solution within 1 hr (Cs^+ capacity: 0.5 mmol/g). Competition studies with both K^+ and Na^+ indicated that these sorbents removed Cs^+ selectively from solutions containing excess K^+ and Na^+.

Planned Activities

In the next 6 months we will further develop the imprint-coating techniques for both Cu^{2+} and UO_2^{2+}. Covalently grafting the functional ligands will also be assessed to link these ligands with the $-Si(OR)_3$ group. Binding studies of these new ligands on sol-gels as well as imprint-coated mesoporous materials, will be performed for Hg^{2+}, Cd^{2+}, UO_2^{2+}, Cs^+, and Sr^{2+}.

Information Access

(1) Dai, S.; Shin, Y. S.; Ju, Y. H.; Burleigh, M. C.; Lin, J. S.; Barnes, C. E.; Xue, Z. "A New Methodology to Functionalize Surfaces of Ordered Mesoporous Materials Based on Ion Exchange Reactions," *Adv. Mater.* 1999, *11*, 1226-1230.

(2) Dai, S.; Burleigh, M. C.; Ju, Y. H.; Gao, H. J.; Lin , J. S.; Pennycook, S.; Barnes, C. E.; Xue, Z. "Hierarchically Imprinted Sorbents for the Separation of Metal Ions," *J. Am. Chem. Soc.* 2000, *122*, 992-993.

(3) Im. H.-J.; Yang, Y.; Allain, L. R.; Barnes, C. E.; Dai, S.; Xue, Z. "Functionalized Sol Gels for Selective Copper(II) Separation," in revision for *Environ. Sci. Technol.*

Removal of Heavy Metals and Organic Contaminants from Aqueous Streams by Novel Filtration Methods

Project ID: 54571

Dr. Nelly M. Rodriguez, Northeastern University

Research Objectives

Catalytically grown carbon nanofibers are a novel material that is produced by the decomposition of selected hydrocarbons over metal particles. The material consists of graphite platelets perfectly aligned and stacked in various directions with respect to the fiber axis. Such an arrangement imparts the carbon nanofibers with a unique combination of physical and chemical properties, including a high electrical conductivity. Perhaps one of the most unexpected findings is that such extraordinarily ordered crystalline solids can exhibit high surface areas, typically ~ 300 m^2/g as grown, which can be enhanced to about 700 m^2/g. Furthermore, by choice of the catalyst and reaction conditions it is also possible to generate structures with different spacing between the platelets, thereby generating new types of sieves. We have developed a process by which it is possible to produce large amounts of nanofibers at the laboratory level, and it is estimated that on a large scale this material could be produced at a cost of ~$1.50/lb, about a tenth of the cost of commercial graphite.

In one section of the program high surface area electrically conductive carbon nanofibers will be employed as the electrode material in the fabrication of unique types of electrochemical filtration and selective collection devices to be used for the removal of heavy metals, radionuclides and transuranic elements from liquid phase effluent streams. Preliminary studies conducted with highly graphitic carbon nanofibers have indicated that the material exhibits a superior performance for the removal of metal ions from low concentration solutions when used as an electrode in an electrochemical cell over that displayed by graphite felts, metal mesh and other forms of conductive carbon. Furthermore, by application of a reverse potential, the metal species that are bound on the nanofiber surface can be rapidly released into a more concentrated solution for eventual recovery or disposal. Having demonstrated the feasibility of this concept for the removal of cadmium, lead and copper species from aqueous solutions both by electroplating and electrosorption methods, we now plan to optimize the performance of the electrode for the removal of metals that are of major concern in the waste streams existing at numerous nuclear production and processing sites. In a complementary series of electrochemical studies the influence of such factors as solution flow rate through the nanofiber bed, variations in bed height and pH of the contaminant solution will be addressed. In this section of the work, efforts will be focused on the removal and collection of such metals as uranium, plutonium, cesium, radium, thorium and strontium.

In a further portion of the project we intend to take advantage of the unique blend of properties of carbon nanofibers for the separation of organic residues including, methylene chloride, tetrahydrofuran, chlorobenzene, toluene, and methylethylketone, from water streams. The approach takes into account the presence of the graphite platelets, that are stacked in a similar manner to a pack of cards, with a minimum interlayer spacing of 0.34 nm that can be expanded by at least 20% without loss of structural integrity. It is anticipated that the organic molecules will be preferentially drawn into the interlayer structure of the nanofibers because of the establishment of a strong interaction of such species with the non-polar basal plane regions of the graphite platelets. We shall also exploit the flexibility of carbon materials with regard to the ability to modify their functionality by suitable treatments. In the present case such treatments will result in a change in polarity of the edge regions of the graphite platelets leading to an enhancement in the wetting of the carbon by the aqueous phase without interfering with the adsorption characteristics of the organic constituent. If desired, the organic compound can be recovered by desorption.

These fundamental studies will provide the rudiments for a large scale process where it is envisioned that removal of organic contaminants from an aqueous stream will be carried out by direct adsorption in the interlayer spaces of the carbon nanofibers in the first stage. Following this step, trace metallic impurities will be trapped on the active edge sites of nanofibers in a series of electrochemical filtration devices. This operation will be achieved by controlled cathode potentials, where increasing negative potentials are applied to a series of carbon nanofiber electrodes and this arrangement functions in a similar manner to a chromatographic column. The sequential application of reverse potentials will then enable each component to be recovered in the "pure" state. This would be an ideal method for purification of contaminated ground water, allowing for the separation of such contaminants as calcium, lead and radionuclides.

Extraction and Recovery of Mercury and Lead from Aqueous Waste Streams Using Redox-Active Layered Metal Chalcogenides

Project ID: 55012

P. K. Dorhout, Colorado State University

S. H. Strauss, Colorado State University.

Research Objective

The goals of this program have been to develop a series of new compounds that act as redox-recyclable heavy metal ion selective materials. This has been a preliminary exploration into the viability of creating materials that act as selective exchange media. We have historically been involved in the separation of ionic pollutants such as radionuclides or toxic heavy metal ions from water by designing extractants with high selectivities and large capacities. We have also recognized that there is a more urgent need to develop processes that allow the target pollutants to be recovered in a minimal volume of secondary waste and that allow the extractants to be reused or recycled. We have been studying redox-active transition-metal-containing extractants that undergo reversible electron transfer activation and deactivation as the target ions are extracted and recovered or that undergo efficient, selective ion exchange.

Research Progress and Implications

The redox-recyclable extractants investigated so far include molecular organometallic complexes such as substituted ferrocenes and layered metal chalcogenides or oxochalcogenides such as MoS_2 and $Zr(HSPO_3)_2$. The molecular complexes can be dissolved in water-immiscible organic solvents for solvent-extraction processes or can be immobilized on inert supports for ion-exchange chromatography. The bulk metal chalcogenide solids themselves function as redox-recyclable or ion-exchangeable materials. We have thus demonstrated in the laboratory the viability of design and function of new compounds that are ion-selective solids or selective composites. The proposed work herein will demonstrate the applicability that these materials possess and will study the effectiveness of these and newly developed materials in complex mixtures of ions and organics.

Using activated MoS_2, greater than 99% of mercury was selectively extracted from an aqueous phase containing 1 M HNO_3 and 10^{-3} M Hg^{2+}, reducing the mercury concentration to ppt levels ($k_D = 10^7$). Greater than 94% of the mercury could be recovered in elemental form after stripping giving an overall reduction in waste volume of more than 10^4. These are just a few examples of how we have been able to effectively design and test materials for selective ion removal from simulated contaminated waste streams.

New compounds developed in our laboratories provide clear-cut evidence that continued efforts in new materials design and synthesis are effective means to solving mixed waste problems. For example, the reaction between aqueous solutions of zirconium or hafnium chlorides and Na_3SPO_3 result in the formation of a high surface-area gel that can be dried into a powder with a composition $M(HSPO_3)_2$ where M = Zr or Hf. These layered materials provide a surface of HS– within the interlayer gallery of the solids that are selective for soft metal cations such as lead, mercury or cadmium when in competition with alkali or alkaline earth ions. A view of these layered galleries is shown in Fig 1. Cadmium can be removed from the solids by washing with mild acid solutions, for example, reconstituting the original solid for reuse. Further modifications of similar materials are under study.

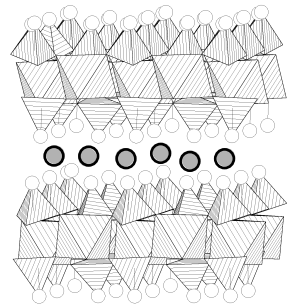
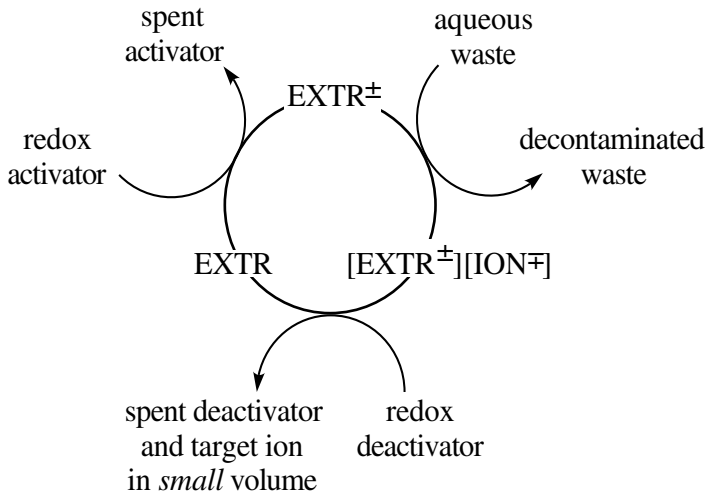


Fig. 1. Cd intercalated $Zr(PSO_3)_2^{2-}$.

In all of our studies, we have examined not only the ion exchange behavior of our compounds but the fundamental processes by which these compounds select, hold, and exchange the ions of interest. These studies have been critical to developing an understanding of the principles that govern the design of new materials for other problems such as mixed hazardous wastes - the focus of this program. For example, we have utilized not only X-ray diffraction techniques for structural elucidation, but we have employed Extended X-ray Absorption Fine Structure techniques to understand how selected contaminant ions such as Hg(II) interact with the host compound matrix. We now believe that the selectivity can be traced to the complex and intimate bonding relationship that exists between the soft cation of choice and the soft anionic matrix which includes coordination geometry and metal oxidation state. Knowledge of these key features has led us to develop new solids such as the zirconium thiophosphate discussed above which is selective for cadmium. This demonstrated expertise will allow our proposed program to be successful at fine-tuning materials that will be selective for specific cations that reside within very complex mixtures.

We have shown, for example, that the complexed mercury in an EDTA-Hg(II) solution can be readily extracted into activated MoS_2 given that mercury ions will prefer the geometric constraints of the solid guest-host Hg_xMoS_2 composite over the organic complex. Indeed, it is likely that our solids will compete favorably over other organic contaminants and naturally occurring complexants that we will encounter in our target mixed waste solutions.

In all, we have been investigating a relatively underexplored strategy in waste remediation, the use of redox-active transition-metal containing extractants for the separation and recovery of specific pollutant cations or anions. We have named this strategy Redox-Recyclable Extraction and Recovery (R^2ER). Our investigations have been based on the seminal electrochemical-switching work of Porter, Martin, Fabbrizzi, Echegoyen, Gokel, Shinkai, and Beer, *but with an added emphasis on recovering*



the target pollutant in a minimal volume of secondary waste. These groups, as well as others, have shown that the binding of ions can be enhanced by electrochemically switching an extractant molecule. However, when one considers practical factors such as duty-cycle time, extractant stability under harsh conditions, extractant effectiveness over many cycles, extractant costs, and secondary-waste volumes, much work needs to be done before useful R^2ER schemes such as ours can be developed and reduced to practice.

Organic Polymer Matrix Studies. The goal of organic polymer matrix processing has been to develop a polymer/extractant mixture that will act to disperse the extractant so as to increase the overall surface area of the absorbing material and to facilitate the regeneration of that material. We have targeted both electrochemically active and inert polymer matrices so as to test the viability of employing electrochemistry as a potential redox-active material switch. Our group has the electrochemical equipment and experience to explore these materials in house.

Recently, we have electrochemically grown films of polypyrrole from a mixture containing a colloid of activated H_xMS_2 particles. This procedure resulted in the encapsulation of layered H_xMS_2 solids within the polymer matrix, as shown in Fig. 2. The encapsulation of materials within polymer matrices is known to occur but no one has studied the ion-exchange ability of these encapsulated materials. We have grown polymer films of polypyrrole from various mixture concentrations of pyrrole and MS_2 suspensions on platinum foil electrodes. The redox activity of the finely-divided extractant on the electrode is currently being established through routine electrochemical methods, and the activity toward our target cations will be determined. The recyclability of the materials will also be demonstrated by electrochemical means. The viability of the electrochemical redox methods will also be demonstrated in solutions that contain mixtures have the organic components of the target systems. Finally, K_D values for the cations of interest will also be determined, where K_D is the

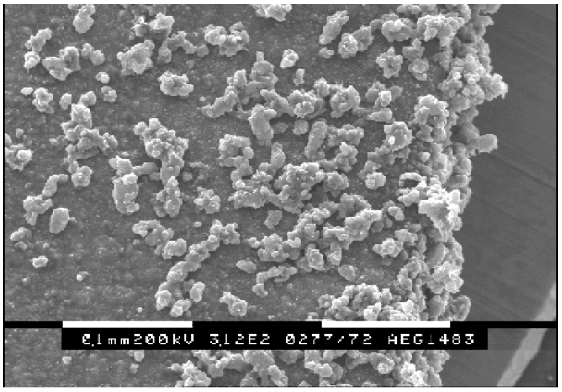


Fig. 2 SEM micrograph of MoS_2 in polypyrrole on a Pt electrode.

ratio of mmole contaminant absorbed per gram of extractant to the mmole of contaminant remaining in solution by volume. These studies will be extended into modified polypyrroles, polyaniline, and polythiophene, each of which has a unique redox couple and region of electrochemical stability, in a given pH range.

Another interesting family of solids are the thiospinels. Thiospinels such as $Cu_2Mn_4S_8$ may be rendered as "porous" ion exchange solids by electrochemically reducing them in the presence of a counter-cation such as Li^+ or Na^+. These solids, shown in Fig. 3, can be reacted with target pollutant mixtures to yield mercury-intercalated solids with $Hg_xCuMn_4S_8$. We are now investigating the electrochemical reactivation of these solids to expel the guest contaminant and reactivate the solid matrix for recycling purposes.

Inorganic Matrix Studies. The goal of sol-gel processing of materials has been to control the structure of that material on a nanometer (macromolecular) scale from the earliest stages of processing.

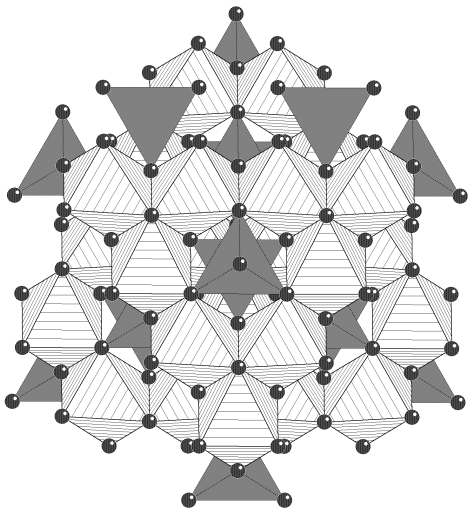


Fig. 3 Polyhedral rendering of $LiCuMn_4S_8$.

Indeed, as precursors to high-surface area ceramics and monoliths, sol-gels offer the ability to prepare high-purity and high-integrity porous or dense ceramics. Sol-gel solids have been shown to be effective materials for supporting and retaining transition metal complexes. We have demonstrated that our MS_2 (M=Mo,W) solids can be encapsulated within a silica matrix and maintain their sorptive abilities. For example, hydrolysis of solution of activated H_xMoS_2 and $Si(OCH_3)_4$ yielded a highly porous material, shown in a transmission electron micrograph, Figure 4, that can readily sorb mercury from aqueous solutions. Figure 4 shows the dark spots, small particles of silicate, large objects, particles of MS_2, and thin veils of silicate surrounding large pores through which solutions can flow unimpeded. Flow studies need to be performed to determine the extent of flow improvement over neat, activated Li_xMoS_2.

In addition to providing a larger surface area for contact of the Li_xMS_2 solids with contaminated solutions, the sol-gel matrix provides stability of the solids by encapsulating the extractant within a matrix. We have shown that the extractant particle size changes over time with activation and deactivation. This is due to the kinetics of intercalation of the contaminant within the extractant matrix - a mechanism that pries apart the layered solids and results in partial exfoliation of the extractant. The gel•MS_2 matrix comprises very small particles of MS_2, as seen in the micrograph, that are nearly single layer. Consequently, exfoliation of the extractant is minimized; thus, the materials do not degenerate with time and create flow and filter problems. It will be important to study the chemistry of these gel materials by selecting several different gels and gel precursors. This can be accomplished by changing the organic oxide in the silicon precursor – methoxy-, ethoxy-, neopentoxy-, for example. These changes effect the gelation time which in turn effects the viscosity

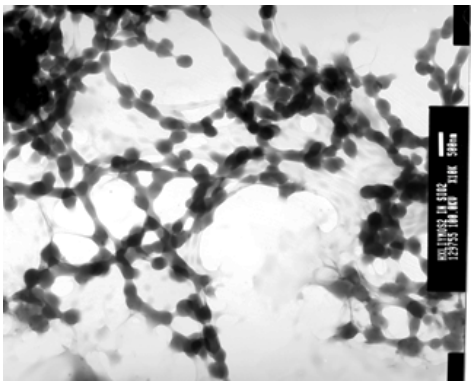


Fig. 4. TEM image of gel•MS_2 matrix showing a large MoS_2 particle in the upper left-hand corner.

of the gel, hence the density of the solid that forms. The density of these sol-gel solids (in the solid phase they are called aerogels or xerogels, depending upon density and preparation) will determine the surface area and flow-through characteristics.

To date, we have explored and have a better understanding of how MoS_2 acts as a redox-active material for selective removal of target ions. We have also explored a family of chalcogenide-based spinel compounds that are also redox active and may be used as electrodes for selective ion exchange. We have placed redox-active solids in conducting polymer matrices and in sol-gel solids as high-surface area supports. Finally, we have begun to design layered thiophosphates that act as very selective ion-exchange solids. Our last efforts on mesoporous solids are not disclosed in this open report as they represent proprietary solids that we are currently disclosing to the patent office.

Manuscripts submitted or in press during the project period:

A. E. Gash, A. L. Spain, L. M. Dysleski, C. J. Flashenreim, A. Kalaveshi, P. K. Dorhout, and S. H. Strauss, "Efficient Recovery of Elemental Mercury from Hg^{2+}-Contaminated Aqueous Media Using Redox-Recyclable Ion-Exchange Materials." *Environ. Sci. Techn.* 1998, *32*, 1007.

P. K. Dorhout and S. H. Strauss, "The Design, Synthesis and Characterization of Redox-Active Materials for the Efficient Extraction of Heavy Element Ions from Aqueous Waste Streams." ACS Symposium Series 727, *Inorganic Materials Synthesis: New Directions for Advanced Materials*, C. H. Winter and D. M. Hoffman, Eds., 1999, 53 - 68.

A. E. Gash, P. K. Dorhout, and S. H. Strauss "Group IV Metal (Zr, Hf) Bis(Hydrogen Monothiophosphate), $H_2M(PO_3S)_2$: Sulfur-Containing Analogs of $H_2M(PO_4)_2$ (M = Zr, Hf) and Their Selective Ion Exchange Properties" *Inorg. Chem.*, 1999, in press.

Manuscripts in preparation at the end of the project period:

A.E. Gash, P. K. Dorhout, S. H. Strauss, P. G. Allen, "XAFS Studies of Soft-Heavy-Metal-Ion-Intercalated M_xMoS_2 (M = Hg^{2+}, and Ag^+) Solids." to be submitted to *Chem. Mater.*

N. Fossé, F. D. Hufford, P. K. Dorhout, S. H. Strauss, "The First Mesostructured Zirconium Thiophosphate and its use for Heavy-Metal Ion Extraction." to be submitted to *Inorg. Chem.*

Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO_2

Project ID: 54942

Joan F. Brennecke, University of Notre Dame

Mark A. Stadtherr, University of Notre Dame
John E. Chateauneuf, Western Michigan University

Research Objectives

The DOE problem addressed by this grant is the separation of organics and radioactive metals from DOE mixed wastes. The objective was to investigate the fundamentals of using supercritical CO_2 to solubilize both volatile organic compounds and metal chelates, with applications to extractions from soils, sludges and aqueous solutions.

The overall objectives of this project were to gain a fundamental understanding of the solubility and phase behavior of metal chelates in supercritical 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. In this project we sought 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 mixed wastes. Our overall program was a comprehensive one to measure, model and compute the solubility of metal chelate complexes in supercritical CO_2 and CO_2/cosolvent mixtures. One aspect of this work was the measurement of local solvation of metal chelates using UV-visible spectroscopy, which provided information on the solution microstructure. We also focused on the measurement of the solubility of metal chelates in supercritical CO_2 and CO_2/cosolvent mixtures, as well as the phase behavior of the chelating agents themselves in CO_2. The purpose of these measurements was to provide information with which we could evaluate and develop thermodynamic models of the solubility behavior. Finally, we focused on the implementation of a more reliable computational technique, based on interval mathematics, to compute the phase equilibria using the thermodynamic models. These studies were undertaken because fundamental information about metal chelate solubility in supercritical 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

The major accomplishments from this project are as follows.

- We have shown that Regular Solution Theory, which is the model used by essentially all previous researchers to estimate the solubility of metal chelate complexes in supercritical CO_2, is totally inadequate. It gives both quantitatively and qualitatively incorrect predictions. Its use for process design purposes would have catastrophic consequences. Rather, we have shown that equation of state models provide a much superior representation of the phase behavior with just one parameter fit to limited metal chelate/CO_2 solubility measurements, as long as some minimal thermodynamic data is available.
- From new solubility measurements, we show for the first time that over a wide range of pressures and temperatures the presence of organic co-contaminants would actually increase the solubility of metal chelates in supercritical CO_2.
- We have demonstrated that on a microscopic level organic co-contaminants that are dissolved in the CO_2 will enrich the immediate area around a solubilized metal chelate complex. However,

in determining the extent to which the metal chelate solubility increases with the addition of co-contaminant, this microscopic behavior is secondary to the solutions' bulk density increase.

– We have developed a completely reliable computational technique, based on interval analysis, to compute the phase behavior of CO_2 mixtures that contain metal chelates and chelating agents using cubic equations of state. Unlike any conventional method (that may be prone to error through failure to converge or convergence to an incorrect solution), the new method that we have developed is guaranteed to provide the correct phase behavior for any particular cubic equation of state model.

Through a combination of phase behavior measurements, spectroscopy and the development of a new computational technique, we have achieved a completely reliable way to model metal chelate solubility in supercritical CO_2 and CO_2/co-contaminant mixtures. Thus, we can now design and optimize processes to extract metals from solid matrices using supercritical CO_2, as an alternative to hazardous organic solvents that create their own environmental problems, even while helping in metals decontamination.

Work on this project is complete. Currently, we are investigating the possible use of specially designed diphosphonic acid ligands for metal solubilization in supercritical CO_2 in collaboration with Argonne National Laboratory and Loyola University – Chicago under DOE EMSP grant DE-FG07-98ER14924.

Information Access

The final report for this grant, including lists of publications and presentations, was submitted for posting on the main DOE EMSP website (http://204.134.132.56/main.htm).

Genetic Engineering of a Radiation-Resistant Bacterium for Biodegradation of Mixed Wastes

Project ID: 60150

Prof. Mary E. Lidstrom, University of Washington

Research Objective

The mixture of toxic chemicals, heavy metals, halogenated solvents and radionuclides in many DOE waste materials presents a challenging problem for separating the different species and disposing of individual contaminants. One approach for dealing with mixed wastes is to genetically engineer the radiation-resistant bacterium, *Deinococcus radiodurans* to survive in and detoxify DOE's mixed waste streams, and to develop process parameters for treating mixed wastes with such constructed strains. The goal for this project is to develop a suite of genetic tools for *Deinococcus radiodurans* and to use these tools to construct and test stable strains for detoxification of haloorganics in mixed wastes.

Research Progress and Implications

This report summarizes work after 2-1/2 years of a 3-year project, during which we have developed a suite of genetic tools for *D. radiodurans*, analyzed *D. radiodurans* promoters, and developed stable expression systems for broad host-range oxygenases.

1. Develop Genetic Tools

Three types of genetic tools have been developed, integration vectors and replicating vectors. These systems are needed to broaden the range of genetic capabilities for manipulating *D. radiodurans* strains, to increase the convenience of working with these strains, and to provide tools to generate constructions that are stable in the absence of selective pressure, a prerequisite for generating process strains.

A. Integration vectors

A series of vectors have been developed that target integration of expressed genes to non-essential sites in the chromosome via double crossover recombination. We have shown that such inserted genes are stable in the absence of selection. The sites that have been chosen and found to be successful are genes encoding amylase and pullulanase. The vectors include derivatives for cloning and expression and for analysis of promoter activity using the two reporters, catechol diooxygenase (XylE) and beta-galactosidase (LacZ). The vectors have also been tested with green fluorescent protein.

B. pI3-based replicating vectors

A second series of replicating vectors have been developed based on the previously reported *D. radiodurans* plasmid, pI3. The plasmid has been completely sequenced and potential replication functions identified by deletion analysis. A minimal replicon has been cloned and used to generate a suite of small and convenient shuttle vectors, including vectors for general cloning, expression, and promoter analysis with LacZ as a reporter. These vectors are useful cloning and screening tools, but are not stable in the absence of antibiotic selection and will not be used for strain construction. A manuscript describing this work has been submitted for publication.

2. Clone and Characterize Promoters

In order to optimize the construction of process strains for biodegradation, a suite of expression systems are needed, preferably regulated and capable of being modulated at different promoter strengths. Since virtually nothing is known about promoters in this strain, we have cloned and characterized a variety of promoters from *D. radiodurans.*

Two different approaches were used to isolate *D. radiodurans* promoters. First, random *D. radiodurans* clone banks were generated in our new promoter screening vector and tested for activity in *E. coli*. Those showing activity were then tested in *D. radiodurans.* This screen resulted in several fragments with promoter activity in both strains. Second, genes were chosen from the genome sequence and the pI3 plasmid that were expected to contain strong promoters, and upstream regions were cloned into the promoter screening vector and tested in both *D. radiodurans* and *E. coli*. A number of promoters showing activity in *D. radiodurans* were isolated in this way, and a subset also showed activity in *E. coli*.

We have mapped transcriptional start sites for several of these promoters and have developed a consensus promoter sequence. Surprisingly, this sequence is similar to the standard *E. coli* σ^{70} promoter sequence, with modifications to the –10 region. A manuscript describing this work has been submitted for publication.

3. Develop Stable Expression Constructs

A subset of these promoters have been used to develop a suite of expression systems for both types of vectors noted above. A series of broad spectrum oxygenases have been cloned into these vectors and are undergoing analysis to determine the range and extent of expression. However, our preliminary data show high activities in some cases, with high stability in the absence of selection for the insertion systems.

Implications

We have developed and tested a suite of tools for genetic manipulation of *D. radiodurans*, including stable expression systems with dynamic promoter ranges, to allow the construction and testing of optimized process strains for biotreatment of mixed wastes. Such strains should be amenable to above-ground treatment scenarios, since they have high level biodegradative capabilities with stable expression.

Planned Activities

1. Complete expression analysis of strains with biodegradative capabilities.
2. Initiate process optimization experiments using artificial waste streams.

Information Access

M. Lidstrom home page: http://faculty.washington.edu/lidstrom

An Alternative Host Matrix Based on Iron Phosphate Glasses for the Vitrification of Specialized Nuclear Waste Forms

Project ID: 55110

Dr. Delbert E. Day, University of Missouri-Rolla

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 34 months of a three year (9/15/96 - 9/14/99) project (DOE Contract # DOE96ER45617). Approximately 350 samples, binary iron phosphate glasses, iron phosphate glasses containing one or more common nuclear waste components such as UO2, Na2O, Bi2O3, Cs2O, SrO, and MoO3, and those containing simulated wastes from the Hanford and Idaho Falls sites have been prepared. The Compositions and melting conditions of these glasses were selected such that the influence of a) the Fe/P ratio, b) valence state of iron ions, c) melting conditions, and d) addition of common waste components on chemical and physical properties and atomic structure of the glasses can be determined. Product Consistency Test and weight loss methods have been used to measure the chemical durability. Redox equilibria between Fe(II) and Fe(III) was investigated using Mössbauer spectroscopy. The atomic structure has been investigated using a variety of techniques including Mössbauer, 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.

Figure 1. PCT determined normalized elemental mass release from three iron phosphate wasteforms containing 35 wt% simulated wastes from Hanford tanks C-112, T-111, and B-110.1 CVS-IS is a borosilicate glass provided by Pacific Northwest National Laboratory.[2] Only those elements for which the mass release is greater than 2 mg/m2.d are shown.

1. Chemical durability

Considerable amounts, in excess of 35 wt% in certain cases, of waste components and simulated wastes which are not well suited for borosilicate glasses can be present in iron phosphate wasteforms with no deterioration in the chemical durability, see Figure 1. The elemental leach rates shown in Figure 1 corresponds to total dissolution rates in the order of 10-10 g/cm^2.min. Such dissolution rates are well within the requirements specified by DOE for a vitrified wasteform.

2. Redox Equilibria

When melted in air at their usual melting temperatures, i.e. 1000 - 1100°C, iron phosphate melts reach a redox equilibria that facilitates glass forming. In general, the addition of most waste components such as Na2O, Cs2O, SrO, and Bi2O3 cause the Fe(II) to increase as compared to the binary iron phosphate glasses. However, none of the waste components or simulated wastes investigated cause the Fe(II) fraction to exceed 0.4, the value above which the glass forming ability of iron phosphate melts is known to decrease. The addition of UO2 results in glasses having smaller Fe(II) fractions. In the case of glasses containing UO2 and a reducing oxide such as Na2O or Bi2O3, the oxidizing nature of UO2 appear to dominate.

3. Atomic Structure

Mössbauer and X-ray absorption spectroscopy show that both species of iron ions are coordinated with 5-5.5 near neighbor oxygen ions. Iron-oxygen coordination does not depend appreciably on the type or the concentration of the waste elements. X-ray photoelectron and Raman spectra of iron phosphate wasteforms suggest that the phosphorus-oxygen network is dominated by (P2O7)-4 dimer units. With increasing waste content, the concentration of the dimer units increase slightly at the expense of the small number of remaining longer phosphate chains. These structural features and results of neutron and high energy X-ray scattering studies suggest that the waste ions are situated outside the second shell coordination environment of iron and phosphorus ions. Consequently, waste ions are unable to seriously influence the chemistry of the -Fe-O-P- network. Therefore, as observed, the addition of waste components does not cause major changes in properties such as the chemical durability of these iron phosphate wasteforms.

4. Crystallization and Glass Forming Characteristics

The glass forming and crystallization characteristics of these glasses change in different ways with different waste components and simulated wastes. In general, the addition of alkali and alkaline earth oxides lead to sharper crystallization peaks which indicate less resistance to crystallization when heat treated at the appropriate temperatures. Knowledge of the valence state of U ions in a vitrified wasteform can help predict the stability of the U ions in the host matrix. Because U6+ is expected to be more mobile than U4+, one prefers to have U4+ in the final wasteform. The energy corresponding to the absorption edge, i. e. the absolute excitation energy (E0), is proportional to the valence state of the absorbing atom. Figure 7 shows the U L(III)-edge XANES data for two reference samples and two iron phosphate glasses containing U. It is evident that the valence state of U in the vitrified wasteforms is IV. In contrast, the addition of UO2 increases the crystallization temperature. However, none of the waste components investigated reduce glass transition and crystallization temperatures below 500 and 600°C, respectively. It must be noted that the measured glass forming and crystallization parameters are well within DOE specifications.

Planned Activities

Comprehensive analysis of the large amount of data that was collected over the last 34 months will be the main focus of the project during remaining few months (a non-funded extension till December 1999 has been requested). In addition, we intend to research and develop melting techniques and laboratory scale melting apparatus that are best suited for processing iron phosphate wasteforms.

References

1. Compositions (wt%): C-112 - 30Fe2O3,45.2P2O5, 10.7UO2, 5.6CaO, 3.3NiO, 2.5Na2O, 1.5Al2O3, 1.0SiO2, and 0.4PbO, T-111 - 30Fe2O3,45.5P2O5, 10.4Bi2O3, 4.0SiO2, 3.6Mn2O3, 2.0Na2O, 1.8La2O3, 1.2UO2, 1.2CaO, and 0.4Al2O3, B-110 - 30Fe2O3, 46.3P2O5, 9Bi2O3, 8.2SiO2, 5Na2O, 0.9Al2O3, and 0.5CaO.
2. Composition (wt%) of CVS-IS is 53.3SiO2, 10.5B2O3, 11.3Na2O, 3.7Li2O, 2.4Al2O3, 7.0Fe2O3, 3.9ZrO2, 1.3 Nd2O3, and 6.6 others.

Information Access

1. Publications

1. "Structural Features of Iron-Phosphate glasses," J. Non-Cryst. Solids, 222 (1997) 144.
2. "Structural Study of Iron Phosphate Glasses", Phys. Chem. Glasses, 38 (1997) 74.
3. "Redox Characteristics and Structural Properties of Iron Phosphate Glasses:A Potential Host Matrix for Vitrifying High Level Nuclear Waste," Ceramic Transactions, 87 (1998) 261.
4. "Chemically Durable Iron Phophate Glass Wasteforms," J. Non-Cryst. Solids, 241 (1998) 1.
5. "On the Structure and Radiation Chemistry of Iron Phosphate Glasses: New Insights from Electron Spin Resonance and Evolved Gas Mass Spectroscopy," Nucl. Inst. Meth. Phys. Res. B, 141 (1998) 600.
6. "Effects of Nuclear Waste Components on Redox Equilibria, Structural Features, and Crystallization Characteristics of Iron Phosphate Glasses," Environment Issues and Waste Management Technologies IV:Ceramic Transactions, 93 (1999) 195.
7. "Iron Redox Equilibria and Crystallization of Iron Phosphate Glasses," Environment Issues and Waste Management Technologies IV:Ceramic Transactions, 93 (1999) 187.

2. Web Access

More information on this research is available at http://www.umr.edu/~gkmars/emsp.html.

Photooxidation of Organic Waste Using Semiconductor Nanoclusters

Project ID: 55387

Dr. J. P. Wilcoxon, Sandia National Laboratories - Albuquerque

Research Objective

Solar detoxification is a process wherein sunlight is captured by a semiconductor particle in suspension to create electrons and holes that then diffuse to the particulate surface to effect the oxidation and reduction of toxic pollutants. Using solar energy to oxidize organic chemicals to carbon dioxide and dilute mineral acids is very energy efficient compared to other methods such as incineration. Finding an efficient particulate has thus been a focus of research, which has had only limited success, the fundamental problem being that materials that efficiently absorb in the visible portion of the solar spectrum also photocorrode.

Past solar detoxification efforts have relied almost exclusively on titanium dioxide, and although it is photostable, it is a *white* material with a UV bandgap that absorbs less than 7% of the solar spectrum. It also suffers from electron-hole recombination in commercially available forms. Recent research has made possible the synthesis of photostable semiconductor nanoclusters with *visible* band gaps that can be tuned by adjusting the cluster size. Thus bulk materials with near IR absorbence edges can be made into visible band-edge materials with stronger redox potentials.

The rate of electron-hole recombination is small in nanoclusters, so they have the potential to act as highly efficient solar detoxification agents. In effect, they act more like molecular organic photoredox catalysts, but with significant advantages in chemical stability because they are inorganic. We propose to investigate the use of these materials in practical detoxification applications, using facilities already in place here at Sandia and at Colorado State University.

Hazardous Gas Production by Alpha Particles in Solid Organic Transuranic Waste Matrices

Project ID: 59934

Dr. Jay A. LaVerne, University of Notre Dame

Research Objective

The objective of this research is to measure the production of hazardous gases like molecular hydrogen and methane produced in the proton, helium ion, and carbon ion radiolysis of selected solid organic matrices such as polymers and resins. The environmental management of mixed waste containing transuranic radionuclei 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. Basic gamma radiolysis studies have been performed on some organic matrices, however, the chemical changes induced by alpha particles and other heavy ions are typically very different and product yields can vary by a large magnitude. Helium ion radiolysis is used to mimic radiolytic conditions in waste materials containing alpha particle emitters while the other particles are useful for obtaining 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 30 months of a three-year project on determining the production of hazardous gases in transuranic waste materials. A major part of the project was to design and build an assembly to measure absolute radiolytic yields in solid organic matrices using accelerated ion beams. The very short range of ions such as alpha particles and the nature of the products place severe limitations on the experimental technique. A special beam exit window assembly coupled to a mass spectrometer has proven to be excellent for monitoring the desired products quantitatively. In addition, the apparatus allows one to determine the diffusion of various gases through polymers.

The first experiments focused on the hydrogen evolution in polyethylene because it is either associated with much of the transuranic waste or it can be used as a model of such waste. Hydrogen is the main gaseous product formed in polyethylene and the present work finds a radiation chemical yield of 3.3 molecules/100 eV of energy absorbed. A gradual increase in hydrogen yield is found with increasing particle linear energy transfer, LET (equal to the stopping power, -dE/dx). The yield of hydrogen with 5 MeV helium ions (LET=97 eV/nm) is 4.5 molecules/100 eV, which is about a 40% increase over that observed with gamma rays. Clearly, hydrogen yields with gamma radiolysis cannot be used to give accurate estimates of yields with alpha particles in the management of waste confinement.

The highest LET carbon ions (10 MeV, 840 eV/nm) give yields of hydrogen from polyethylene of 5.7 eV/100 eV. Methane yields in polyethylene are about two orders of magnitude less than that of hydrogen. The mechanism for gas formation in particle tracks is not well understood, and further experiments are examining the polymer cross-linking and scission in order to elucidate the formation processes. The hydrogen diffusion coefficient in polyethylene is found to be 2.2×10^{-6} cm^2/s, which is about an order of magnitude less than that found in typical hydrocarbon liquids. Diffusion of gases is a vital parameter in many engineering designs.

Gaseous product yields have also been determined in the proton, helium ion, and carbon ion radiolysis of polypropylene, poly(methyl-methacrylate) (Plexiglas), and polystyrene (Styrofoam). Gamma radiolysis of these materials gives hydrogen yields of 2.58, 0.24, and 0.04 molecules/100 eV, respectively. The large decrease in yields is obviously due to the nature of the side group connected

to the main carbon-carbon polymer backbone, but the mechanism is not known. Irradiation with particles of higher LET can lead to dramatic increases in hydrogen yields. For instance, the molecular hydrogen yields for 5 MeV helium ions are 3.15, 0.62, and 0.15 molecules/100 eV for polypropylene, poly(methyl-methacrylate), and polystyrene, respectively. The increase for polypropylene is only about 20% while that for polystyrene is about 400% from gamma rays to 5 MeV helium ions. It is obvious that relative yields for one type of polymer cannot be reliably substituted for another. Such a result is completely unexpected and could lead to important engineering decisions concerning the management of radioactive materials containing these polymers.

Planned Activities

Many important experiments still need to be performed on the formation and evolution of gases in polyethylene, polypropylene, poly(methyl-methacrylate), and polystyrene. These materials are commonly found in construction materials and they invite interesting fundamental questions. Other products such as methane, acetylene, and carbon monoxide are observable in some of these materials. An examination of their dependence on particle LET may give information on the mechanisms involved. Hydrogen production in other important polymers, such as polyvinyl alcohol, polypyridine, and polybutylene are in progress. Polypyridine (Reillex) is a common resin used in the extraction of transuranic waste materials. Hydrogen yields from it show a large dependence on particle type, which is not currently being addressed.

Experiments are also underway to determine the source of the observed LET dependence on hydrogen yields. Polymer chain scission and crosslinking may give some indication of the reactions leading to and subsequent to the formation of hydrogen. Infrared and UV absorption experiments will also give some indication of the fate of the polymer chain following irradiation. These experiment are vital if one is to be able to predict the production of gaseous products in the radiolysis of polymers.

Information Access

Z. Chang and J. A. LaVerne, Molecular Hydrogen Production in the Radiolysis of High-Density Polyethylene, J. Phys. Chem. B, 103, 8267, 1999.

Z. Chang and J. A. LaVerne, Hydrogen Production in γ-ray and Helium Ion Radiolysis of Polyethylene, Polypropylene, Poly(methyl-methacrylate) and Polystyrene, J. Poly. Sci. in press.

J. A. LaVerne, Z. Chang and M. S. Araos, Heavy Ion Radiolysis of Organic Materials, Radiat. Phys. Chem. submitted.

Z. Chang and J. A. LaVerne, Hydrogen Production in the Heavy Ion Radiolysis of Polymers: I. Polyethylene, Polypropylene, Poly(methyl-methacrylate) and Polystyrene, Macromolecules, submitted.

The Adsorption and Reaction of Halogenated Volatile Organic Compounds (VOCs) on Metal Oxides

Project ID: 55115

Dr. Jack Lunsford, Texas A&M University at College Station

Research Objective

The goal of the research is to elucidate the properties of the material responsible for the activation of halocarbons and the nature of the intermediates formed in the dissociative adsorption of this general class of compounds. This information is essential for interpreting and predicting stoichiometric and catalytic pathways for the safe destruction of halocarbon pollutants. The specific research objectives are: (1) to study the adsorption and reactivity of chloromethanes, chloroethanes, and chloroethylenes on basic, neutral, and acidic oxides, including magnesium oxide, chromium oxide, silica, alumina, silica-alumina, and iron and cobalt oxides, both supported and unsupported; (2) to identify the reaction intermediates of the above halocarbons by Raman spectroscopy, NMR methods, and infrared reflection absorption and high resolution electron energy loss spectroscopies (IRAS and HREELS, respectively); (3) to define rate laws and kinetic models for the reaction of the above halocarbons with O_2 on oxides surfaces; (4) to investigate the effect of H_2O on the selectivity with respect to formation of Cl_2 and HCl; and (5) to determine the role of adsorbed oxygen and chlorine as poisons for halocarbon activation on oxides.

Processing of High Level Waste: Spectroscopic Characterization of Redox Reactions in Supercritical Water

Project ID: 54828

Dr. Charles A. Arrington, Jr., Furman University

Research Objective

We are engaged in a collaborative research effort with Los Alamos staff scientists Steven Buelow and Jeanne Robinson, 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 own work has been focused on a careful kinetic study of oxidation reactions of hydrogen peroxide with chromium hydroxide. This reaction occurs readily at ambient temperatures.

Research Progress and Implications

Most of the work during the second year of the grant was carried out at Los Alamos National Lab. During the summer of 1998 the PI and two undergraduate students from Furman worked for 10 weeks at Los Alamos National Laboratory. David Pond graduated from Furman in May, and Ginger Denison is a rising senior who is working at LANL again in the summer of 1999. We are now able to carry out experiments using the new Raman system recently installed at Furman. Two students, David Pond and Robb Lanning, who worked on the project in 1997, continued their research for one semester at Furman during the 1998-99 academic year.

We began work with a new high pressure diamond-window cell machined from Inconel. The diamond windows are seated using gold gaskets. We were never able to get a seal to hold above 374 °C. The Inconel may be too hard to provide a seal at higher temperatures or the coefficient of thermal expansion may be too large. As a result of the shortcomings of this cell we devoted our attention to two sets of experiments that could be carried out at ambient temperatures: kinetics of the reaction of chromium hydroxide with hydrogen peroxide in basic solution, and spectroscopy of the hydroperoxide anion, HO_2^-.

Ginger Denison carried out an extensive set of experiments using UV-visible spectroscopy to lower the production of chromate ion, CrO_4^{2-}, the product of oxidation of $Cr(OH)_4^-$ by H_2O_2 in basic solutions. The reactions were carried out under pseudo first order conditions with OH^- and H_2O_2 present in excess. The rate of reaction was found to depend on the aging of the chromium hydroxide solutions, getting slower the longer the solution ages before reaction. We attribute this behavior to oligomerization of the chromium hydroxide solution. The decay of chromium hydroxide concentration with time cannot be fit to a single exponential function. We get good fits of the data to two or three exponential functions. Such behavior is consistent with different degrees of polymerization leading to forms of the hydroxide that react at different rates– slower rates at higher degrees of polymerization. The rate of reaction was found to decrease with increasing concentration of hydroxide ion under our experimental conditions. The rate initially increased with increasing hydrogen peroxide concentration, but at the higher concentrations of H_2O_2 the rate of reaction decreases. The reaction was carried out over a temperature range from 15 to 25 °C. The Arrhenius plot of these data gives an activation energy of 53 kJ/mol. The rapid reaction of chromium hydroxide at room temperature makes this reaction promising as a means of treating Hanford tank wastes which are high in chromium concentration.

The second set of experiments has grown out of our observation of the O-O stretching vibration in the Raman spectrum in the solutions prepared for the kinetic studies. In the presence of OH^- a new Raman band appears at 850 cm^{-1}. We identify this band as the O-O stretch of the hydroperoxide anion. Because hydrogen peroxide is a stronger acid than water, HO_2^- is the dominant form of hydrogen peroxide in basic solution. In understanding the mechanism of oxidation by hydrogen peroxide it is important to determine whether H_2O_2 or HO_2^- is the actual oxidizing agent in the reaction with chromium hydroxide. We have not yet carried out experiments to answer this question. We have examined the Raman spectrum of aqueous solutions of HO_2^- formed by reaction of OH^- with H_2O_2 and Na_2O_2 with H_2O and with D_2O. Evaporation of these solutions provides crystalline solids, for which we have obtained infrared and Raman spectra. There is very little information in the literature on the vibrational spectroscopy of HO_2^-. Extensive *ab initio* calculations have been carried out to support this assignment. These calculations show that the O-O stretch and HOO bending modes are mixed, especially in the deuterated species. We see no shift in the 850 cm^{-1} band on deuteration. The strong mixing with the bending mode may be responsible for the coincidence of these two frequencies. Similar mixing of these normal modes has been reported for the neutral hydroperoxide radical, HO_2. The calculations also suggest that hydrogen bonding of hydroperoxide with water reduces the electron density on the anion with a resulting increase in the frequency of the O-O stretch.

Planned Activities

During the summer of 1999 two students will work with the PI at LANL. We will continue to investigate the kinetics of oxidation of Cr(III) in basic solution using hydrogen peroxide as the oxidizing agent. We plan to determine the multi-exponential rate constants for samples with different aging histories covering periods up to several weeks of aging. We also will study the rate of consumption of hydroxide ion using a pH meter to follow $[OH^-]$. The third reactant, hydrogen peroxide can be followed by its characteristic O-O stretching vibration in the Raman spectrum. Monitoring each of the reactants separately under pseudo first order conditions will provide a complete understanding of the factors that affect the rate of dissolution of chromium (III) species by hydrogen peroxide in basic solutions.

Cr(III) species in Hanford tank wastes have not been quantitatively characterized, but it is certain that some of the chromium is in the form of the oxide. For this reason we will examine reactions with Cr_2O_3, which is insoluble and unreactive with hydrogen peroxide at ambient temperature. We will look for reaction at higher temperatures and in the presence of catalysts. Also we plan to carry out experiments using sonication to promote reaction.

Information Access

Three students have given talks at the Southeast Regional ACS meeting and the National Conference of Undergraduate Research. Two posters will be presented at the ACS meeting in New Orleans on August 22, 1999. Poster material is being submitted with this report. Senior papers by Dana Olsen and David Pond are available from the PI. A manuscript on HO_2^- is in preparation.

Fundamental Chemistry and Thermodynamics of Hydrothermal Oxidation Processes

Project ID: 55276

Dr. John M. Simonson, Oak Ridge National Laboratory

James G. Blencoe, Oak Ridge National Laboratory
Sheng Dai, Oak Ridge National Laboratory
Ariel A. Chialvo, Oak Ridge National Laboratory
Peter T. Cummings, University of Tennessee

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. Focus areas for this project include measurements of the solubility and speciation of actinides 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.

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 during 2.5 years of this three-year project.

Fluid-Phase PVT Properties and Fluid+Fluid Phase Equilibria. The unique, high pressure vibrating-tube densimeter (VTD) was used to measure the densities of CO_2-N_2-H_2O fluids at 300°C, 8-100 MPa. Sufficient data were collected to tightly constrain the volumetric properties of each aqueous binary subsystem, and for the ternary system. A draft manuscript that presents and describes the volumetric data we obtained for N_2-H_2O mixtures has been prepared for submission to *Contributions to Mineralogy and Petrology*. The VTD was also used to obtain *L-V* data for binary and ternary CO_2-N_2-H_2O fluids from 300 to 350°C. Some of these data are tabulated in the manuscript we have prepared that describes our vibrating-tube technique for locating the *P-T-X* positions of *L-V* phase boundaries in mixed-volatile systems (see below). The remaining data, and additional *L-V* data we plan to acquire in the next few months, will be presented in papers we will write on *L-V* relations in (a) the CO_2-N_2-H_2O system at 300°C, and (b) the CO_2-H_2O and N_2-H_2O systems at 300-367°C.

No published equation of state for CO_2-H_2O mixtures accurately predicts the volumetric properties of these fluids at temperatures between 300 and 400°C. During this past year new types of equations for modeling the thermodynamic mixing properties of mixed volatile fluids were developed and tested. We have discovered that an empirical excess pressure equation accurately represents the excess molar volumes of CO_2-H_2O mixtures at 400°C, 10-400 MPa. We have also found that a modified Lee-Kesler (MLK) equation can be used to represent volumetric properties, using our excess molar volume data for 400°C to evaluate cross-virial coefficients. Excess molar volumes for 10-100 MPa calculated from the resulting expression are as accurate as those obtained from the excess pressure

equation described above. The next task in this line of investigation is to assess the ability of the MLK equation to accurately represent the volumetric properties of CO_2-H_2O fluids at 400°C, 0-10 and 100-400 MPa.

Finally, a manuscript describing the vibrating-tube technique for delimiting liquid-vapor fields in mixed-volatile systems at elevated temperatures and pressures has been prepared. The method is highly precise and accurate, and in the article we present the data we have obtained that tightly constrain the *P-X* limits of the *L-V* regions in the CO_2-H_2O and N_2-H_2O systems at 300 and 350°C.

Solubility measurements. Methods were developed to measure conveniently for the first time solubilities of uranium oxide and related carbonates in aqueous solutions at elevated temperatures and to establish spectroscopic techniques to identify the solid uranium-containing phases in equilibrium with the fluid. Our main experiments focused on solubilities in (carbonate + bicarbonate) buffered solutions with and without additional NaCl. Three methods have been applied in these studies. A conventional quenching method, in which (solid + liquid) samples are sealed in fused quartz tubes and equilibrated at elevated temperature with subsequent quenching to room temperature and analysis of solution, has been used at temperatures to ~150°C. A second method involving continuous monitoring of uranyl species in solution at high temperature by ultraviolet-visible spectrophotometry has also been developed in this program. The key to this method lies in the use of modified commercial micro-scale flow cells that can be thermostated directly in the beam of the spectrophotometer. This setup is expected to permit measurements on aqueous solutions up to 400°C. High temperature autoclaves equipped with gold bags have also been used. In this method the (solid + liquid) sample is contained within a flexible gold bag in the autoclave, with external pressure applied by adding water to the annulus between the bag and the autoclave. The system is thermostated in a rocking furnace, and filtered liquid samples are withdrawn at intervals for analysis.

Early analysis by X-ray diffraction of the solid phase recovered from equilibrium experiments indicated that the phases produced at the high temperatures were amorphous. This prompted us to choose micro-scale diffuse reflectance Fourier-transform infrared spectroscopy (DR IR) as a primary technique to analyze structures of these solid phases. The possible solid phases are UO_2CO_3 and $Na_4UO_2(CO_3)_3$. It was found that the $Na_4UO_2(CO_3)_3$ solid phase is not stable at 120°C in carbonate buffer solution. Our experiments indicate that the solubilities of UO_3 and $Na_4UO_2(CO_3)_3$ are governed by the hydrolysis reaction at high temperature (>100°C). The strong complexation capability of carbonate anion plays little role in this process. Similar observations were made concerning the UO_2CO_3 system. This prompted us to investigate hydrolysis reactions involving uranyl species at elevated temperature. We used factor analysis (FA) and self-modeling (SM) as a new methodology to study uranyl uv-vis absorption spectral variations induced by temperature changes. Information concerning speciation and thermodynamic reaction enthalpy was also obtained. The main results have been published in *Radiochimica Acta.*

The solubility of UO_3(s) in 0.1 M carbonate buffer ($NaHCO_3/Na_2CO_3$) was measured as a function of temperature and ionic strength (as NaCl) from 112 to 149°C. It was found that the solubility decreased with increasing temperature. DR IR spectra of the solids from high temperature exhibited signals characteristic of polymeric species. This indicates that the solid phase may convert from UO_3 to the polymeric species because of the hydrolysis reaction of uranyl ion at elevated temperature in basic solutions. Our spectroscopic analysis of solid phases indicates that the $Na_4UO_2(CO_3)_3$ solid phase is stable at temperature < 100°C. The solubility in the 0.1 M buffer solutions decreases with temperature.

Molecular Dynamics Simulation Studies of Aqueous Systems at High Temperatures. Molecular simulation of HCl solutions was initiated, with particular emphasis on the modeling of the hydronium ion. We performed potential of mean force calculations for aqueous HCl solutions, based on the SPC/E model of water and Fornili's model for hydronium ion, toward the calculation of the association constant of HCl at near-critical conditions. We then modified the corresponding molecular dynamics codes to run the above system based on another type of hydronium ion potential model (Kusaka et al.), currently being used for the potential of mean force calculations.

We applied the Chialvo-Cummings solvation formalism to model electrolyte solutions, based on integral equation calculations of simple alkali halides. We tested a regression hypothesis currently

used by experimentalists, and interpreted the microscopic mechanism behind its success. A portion of this work is included in a manuscript under submission, and a poster to be presented in the 4th. Liquid Matter Conference (Spain, July 1999).

Planned Activities

Activities for the remainder of this project will focus on completion of research in progress as described above, and preparation of manuscripts for presentation and publication.

Information Access: Publications

Blencoe, J. G., Anovitz, L. M. and Seitz, J. C., 1998, A Helmholz Free Energy Model for Supercritical H_2O-CO_2 Mixtures. *Geol. Soc. Amer. Abs. with Prog*., V. 30, p. A-319.

Blencoe J. G., Seitz J. C., and Anovitz L. M., 1999, The CO_2-H_2O System. II. Calculated Thermodynamic Mixing Properties for 400°C, 0-400 MPa. *Geochim. Cosmochim. Acta*, V. 63, in press.

Blencoe, J. G.; Anovitz, L. M.; Seitz, J. C. (1997) "Serious shortcomings of semi-empirical equations of state for high-temperature aqueous C-O-H-N fluids," *Geol. Soc. Amer. Abs. with Prog.* 29, A-210.

Blencoe, J. G.; Anovitz, L. M.; Seitz, J. C. (1998) A New Method for Modeling the Thermodynamic Mixing Properties of High-Temperature H_2O-CO_2 Fluids. *Eos*, V. 79 (in press).

Chialvo, A. A.; Cummings, P. T.; Simonson, J. M.; Mesmer, R. E. (1998) "Thermodynamics and kinetics of ion speciation in supercritical aqueous solutions: A molecular-based study," *Fluid Phase Equilibria* 150-151, 107-115.

Chialvo, A. A.; Cummings, P. T.; Simonson, J. M.; Mesmer, R. E. (1999) "Solvation in high-temperature electrolyte solutions. I. Hydration shell behavior from molecular simulation," *J. Chem. Phys*. 110, 1064-1074.

Chialvo, A. A.; Cummings, P. T.; Simonson, J. M.; Mesmer, R. E. (1999) "Solvation in high-temperature electrolyte solutions. II. Some formal results," *J. Chem. Phys*. 110, 1075-1086.

Chialvo, A. A., Cummings, P. T., Simonson, J. M. and Mesmer, R. E., "Solvation in High-Temperature Electrolyte Solutions," *J. Molec. Liquids*, submitted for publication (1999).

Chialvo, A. A., Kusalik, P.G., Cummings, P. T., Simonson, J. M. and Mesmer, R. E., "Molecular Approach to High Temperature Solvation . Formal, Integral Equation, and Experimental Results" *J. Phys. Condensed Matter*, submitted for publication (1999)

Dai, S.; Burleigh, M.; Simonson, J. M.; Mesmer, R. E.; Xue, Z.-L. (1998) "Application of chemometric methods in UV-Vis absorption spectroscopic studies of uranyl ion dimerization reaction in aqueous solutions", *Radiochimica Acta* 81, 195-199.

Dai, S. and Simonson, J. M., "High-temperature UV-VIS spectra of uranium carbonate complexes", in preparation (1999).

Moore, R. C.; Mesmer, R. E.; Simonson, J. M. (1997) "The solubility of potassium carbonate in water between 384 and 529 K measured using the synthetic method," *J. Chem. Eng. Data* 42, 1078-1081.

Seitz, J. C.; Blencoe, J. G. (1997) "Experimentally determined volumetric properties and solvus relations for H_2O-CO_2-N_2 mixtures at 300°C and pressures < 1000 bars," *Geol. Soc. Amer. Abs. with Prog.* 29, A-209.

Seitz J. C., and Blencoe J. G., 1999, The CO_2-H_2O System. I. Experimental Determination of Volumetric Properties at 400°C, 10-100 MPa. *Geochim. Cosmochim. Acta,* V. 63, in press.

Seitz, J. C., Blencoe, J. G., Singh, J., and Anovitz, L. M. 1999, A Vibrating-Tube Technique for Determining the Pressure-Temperature-Composition Limits of Liquid-Vapor Fields in Mixed-Volatile Systems. *Amer. Mineral.,* in internal review.

Singh, J., Blencoe, J. G., and Seitz, J. C., 1998, Experimentally Determined Excess Molar Volumes for H_2O-N_2 Fluids at 300°C, 75-1000 Bars. *Geol. Soc. Amer. Abs. with Prog.,* V. 30, p. A-319.

Singh, J., Blencoe, J. G., and Seitz, J. C., and Anovitz, L. M., 1999, The H_2O-N_2 System: Experimental Determination of Volumetric Properties at 300°C and 75-1000 Bars. *Contrib. Mineral. Petrol.,* in internal review.

Several presentations at conferences and meetings have also been made on this project.

Acid-Base Behavior in Hydrothermal Processing of Wastes

Project ID: 54506

Dr. Keith P. Johnston, University of Texas at Austin

Peter Rossky, University of Texas at Austin

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.

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 third year of a 3-year project, which has been extended to include a fourth year. Many of the DOE wastes contain high concentrations of nitrates, and the equilibrium of these species is of interest in hydrothermal oxidation. To address this, UV-Vis spectroscopy was utilized to measure the decomposition of aqueous HNO_3 solutions above 300 ºC, in some cases with added NaOH, H_2O_2, and/or $NaNO_2$, to form NO_2, HNO_2, NO, N_2O and oxygen. Optimization models have been developed to determine equilibrium constants from the spectra for dissociation, redox and disproportionation reactions involving nitric and nitrous acid, NO_2, NO, N_2O, NO_3^-, and oxygen in supercritical at temperatures of 380°C and 400°C and at pressures of 276 to 414 bar. A constrained nonlinear programming (NLP) model of moderate size has been developed to estimate equilibrium constants and extinction coefficients. This model is optimized using an implementation of the generalized reduced gradient (GRG) algorithm. Although it was only possible to measure the absorbance of two of the twelve species by UV-Vis spectroscopy, six equilibrium constants and two extinction coefficients could be optimized . Significant improvements of these values are obtained with a Jackknife Statistical implementation. Linear extrapolation of the log K

versus density plots to zero density results in values which are very close to independent gas-phase values.

On the theoretical side, we have completed a very important simulation study of ion transport in water under extreme conditions and also initiated a highly novel investigation of hydrolysis reactions in SCW.

The motivation for the study of transport is based on the facts that 1) transport coefficients are fundamental to solution reaction rates, but the behavior of such transport properties over wide ranges of density and temperature are not well understood, and 2) ionic association equilibria under extreme conditions in SCW is typically accessed indirectly via interpretations of conductivity measurements through ion pairing models. Although there is some variation, results suggest a linear increase in ionic diffusion constant with decreasing density at higher densities, turning over to a plateau in the most interesting region of SCW densities. We have for the first time developed a complete physical explanation of the conductivity data, using computer simulation to analyze the transport coefficients. We have demonstrated that the plateau in the data is reproduced computationally and is associated with an increasing imbalance between water-water forces and the stronger solvent-solute forces acting on the solvent in the ionic hydration shell. This shell remains intact throughout the measured density region but exerts an increasing friction on the ion with decreasing density. At densities below those measured experimentally to date, the hydration shell does begin to degrade, in accord with our earlier interpretation as solvent adsorption, and the transport rate is predicted to resume an increase. Of perhaps most importance, the calculated results have led to a suggested manner in which to analyze purely experimental data in order to best elucidate the physical content. The results of this work are currently being prepared for publication.

Planned Activities

We plan to study carbonate/bicarbonate/ carbonic acid equilibria in supercritical water as these species play a central role in hydrothermal oxidation. Chemical equilibria for these species will be monitored with novel pH indicators developed in our lab. The behavior of the equilibrium constants will be analyzed in terms of our previous studies of ion solvation in supercritical water.

We have initiated modeling and simulation of aqueous hydrolysis reactions in SCW due to their ubiquitous presence in SCW oxidation reactions. Under ambient aqueous conditions, the first step of an S_N1 reaction occurs by initial separation into an *ion* pair, with typical further reaction of a carbocation. However, the relative stability of the ion pair and the alternative reaction path involving separation into a *neutral* radical pair depends very directly on the solvent polarity. Even in ambient water, it has been demonstrated that a free energy barrier to separation arises due to the transition from a covalent to a separated ionic state. As is widely appreciated in other contexts, SCW offers *tunable* polarity. Thus, one should expect not only that reaction barriers depend on solvent density, but also that the underlying mechanism itself will vary. In order to understand this variation in mechanism in detail, we are in the process of investigating the active mechanism and free energy associated with dissociation of the model reactant, t-butyl chloride. The details of dissociation of this model system have been studied theoretically in considerable detail in ambient water in the past, so there is an excellent base of models from which to start.

Information Access

(1) Chlistunoff, J. B. ; Johnston, K. P. UV-Vis Spectroscopic Determination of the Dissociation Constant of Bichromate from 160°C to 400°C. *J. Phys. Chem. B.* **1998,** *102*, 3993-4003.

(2) Chlistunoff, J. B.; Ziegler, K. J.; Lasdon, L. ; Johnston, K. P. Nitric/Nitrous Acid Equilibria in Supercritical Water. *J. Phys. Chem. B.* **1999,** *103*, 1678-1688.

(3) Johnston, K. P. ; Chlistunoff, J. B. Neutralization of Acids and Bases in Subcritical and Supercritical Water: Acetic Acid and HCl. *J. Supercritical Fluids*. **1998,** *12*, 155-64.

(4) Ziegler, K. J.; Lasdon, L.; Chlistunoff, J. ; Johnston, K. P. Optimization Models for Determining Nitric Acid Equilibria in Supercritical Water. *Computers and Chemistry*. **1999,** *in press.*

(5) Johnston, K. P. ; Rossky, P. J. Solution Chemistry in Supercritical Water: Spectroscopy and Simulation. In *NATO Adv. Study Institute on Supercritical Fluids*; E. Kiran, Ed.; 1999, in press.

The Sonophysics and Sonochemistry of Liquid Waste Quantification and Remediation

Project ID: 54897

Dr. Thomas J. Matula, University of Washington

Executive Summary

When an ultrasonic field of moderate to large intensity is applied to a liquid, the liquid often fails under the action of the dynamic tensile stress applied by the ultrasound. Consequently, the vapor cavity that is formed during the rarefaction portion of the sound field can thus grow rapidly so long as the applied negative acoustic pressure exceeds the vapor pressure of the liquid; subsequently, however, this cavity is driven into an implosive collapse as the sound field turns positive and applies a compressive force to the cavity. Because of surface tension, the cavity remains spherical for much of its life cycle and, accordingly, an enormous energy concentration—as much as 12 orders of magnitude—can result from this growth and collapse sequence—a phenomenon called acoustic cavitation. The temperatures and pressures experienced by the material contained within the imploding cavities can achieve values in excess of tens of thousands of degrees and tens of kilobars, respectively. These high temperatures and pressures can act as an intense microreactor and induce a variety of chemical reactions; the ability of these reactions to induce a particular effect is called sonochemistry, and holds high promise as a specific chemical approach to waste contaminant remediation.

A variety of investigators have demonstrated the utility of the sonochemical reactor; for example, the natural half-life of parathion, a pesticide of widespread use, is 108 days. Under ultrasonic irradiation at 20 kHz in deionized water, all of the initial parathion is degraded in less than two hours; ultrasonic irradiation in an aqueous solution containing the highly toxic pentachlorophenate (PCP) results in the almost complete degradation of PCP in about 100 minutes; researchers have also found that acoustic irradiation of chlorinated C1 and C2 volatile organic compounds (VOCs) resulted in a VOC destruction of up to 99.9% in less than an hour.

Although sonochemistry holds such high promise for use in waste contaminant remediation, the principal mechanism that leads to chemical degradation, acoustic cavitation, is a complex and difficult to understand phenomenon. Chemists who are performing experiments in sonochemistry know little of acoustic cavitation and how to use it in an optimal way; physicists who know something about cavitation bubble dynamics don't understand the chemistry. Indeed, the President of the European Society of Sonochemistry has deemed this field a "black art", whose progress is mainly empirical, and which will lack credibility as a mature science until multidisciplinary teams involving both physicists and chemists examine the problem from a fundamental viewpoint. We propose a systematic study of the phenomenon of acoustic cavitation as it applies to sonochemistry, and especially as it applies to waste contaminant remediation.

Research Progress and Implications

We have established a multidisciplinary team involving internationally recognized experts in the field of acoustic cavitation from the Applied Physics Laboratory at the University of Washington; they will be joined by experts in the field of industrial/analytical chemistry from the Center for Process Analytic Chemistry, also at the University of Washington; participating as consultants are recognized experts from Lawrence Livermore National Laboratory, Savannah River Technology Center, Pacific Northwest National Laboratory, and the University of California, Irvine. Finally, the University of Washington itself plans an extensive and comprehensive research program in this general area.

Research Objective

We propose 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, and to determine the optimal acoustical parameters in the use of sonochemistry for liquid-waste-contaminant remediation.

Measurements and Models for Hazardous Chemical and Mixed Wastes

Project ID: 60155

Dr. Cynthia Holcomb, National Institute of Standards and Technology
Dr. Laurel A. Watts, National Institute of Standards and Technology

Dr. Breverly Louie, National Institute of Standards and Technology
Stephanie L. Outcalt, National Institute of Standards and Technology
Michael E. Mullins, Michigan Technological University
Dr. Tony N. Rogers, Michigan Technological University
Dr. Andrew A. Kline, Michigan Technological University

Research Objectives

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 June 1999, seventeen months into the a three year project, we have made significant progress in the database development, have begun testing the models, have completed the pure component measurements, and have been measuring selected binary mixtures.

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 permittivities 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. The database has been extended to over 250 data publications and over 100 modeling publications. The database will continue to be updated. These data have been used to determine what compositions and temperatures are needed to complete and validate the data for each binary mixture. Very little data has been reported for the acetone+isopropyl alcohol system. More extensive measurements will be required for this system.

Model Development: Two models are being investigated 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 model 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 model has been tested with pure solvents, solvent mixtures and solvent mixtures with salt. The model performs well predicting the vapor pressure and vapor composition, given the temperature and liquid composition, for pure solvents and solvent mixtures. Initial results for mixtures containing salt are encouraging.

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 pure component measurements are completed. The new ebulliometer at MTU is complete. Currently, gravimetrically prepared aqueous-solvent and solvent-solvent mixtures are being prepared and measured in the ebulliometer. The sampling system for the phase equilibria apparatus at NIST is being validated with gravimetrically prepared mixtures. Measurements on the aqueous-solvent and solvent-solvent mixtures are in progress. The measurements will cover a temperature range from 275 to 425K. Due to the scarcity of data, more extensive measurements will be performed on the acetone+isopropyl alcohol system.

Planned Activities

Upon completion and verification of the aqueous-solvent and solvent-solvent mixture measurements, the VLE, activity coefficients, and densities of the aqueous+solvent+salt mixtures will begin. All measurements will be completed within the next year. The data will cover the temperature range from 275 to 425 K at pressures to 14 MPa. In the final six months of this project, the data will be used to optimize and test the models developed at NIST and MTU. The remaining tasks are listed below:

- Complete bubble-point pressure, coexisting density, and compressed liquid density measurements on aqueous+solvent and solvent+solvent mixtures.
- Measure bubble-point pressures, coexisting densities, and compressed liquid densities for aqueous+solvent+salt mixtures.
- Test the model predictions for mixtures.

Reference

[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.

Isolation of Metals from Liquid Wastes: Reactive Scavenging in Turbulent Thermal Reactors

Project ID: 60326

Dr. Jost O.L. Wendt, University of Arizona

Dr. William P. Linak, National Risk Management Research Laboratory (NRMRL)
Dr. Alan R. Kerstein, Sandia National Laboratories - California
Dr. Arne J Pearlstein, University of Illinois at Urbana-Champaign
Dr. Alexander Scheeline, University of Illinois at Urbana-Champaign

Research Objectives

A large portion of the Department of Energy (DOE) radioactive waste inventory is composed of metal-bearing liquid wastes, which may or may not also contain organics. It is highly desirable to concentrate the metals in order to reduce the volume of these wastes and to render them into an environmentally benign form. One method for doing this is to exploit high-temperatures to reactively capture metals by sorbents, and thus to isolate them from the environment. The objective of this research is to provide the background information necessary to design a process that accomplishes this on a large scale, namely in hot turbulent flows, into which are injected the wastes to be treated and, also the sorbents that scavenge the metals. The current work focuses on cesium and strontium, which are present in the DOE inventory as radioactive isotopes.

The project involves five investigators at three institutions, and is comprised of the following parts:

1) Experimental research at the University of Arizona focuses on the chemistry of cesium and strontium sorption on kaolinite and lime sorbents in a laminar flow environment.
2) Theoretical research pursued jointly by the University of Arizona and Sandia Laboratories, Livermore, focuses on prediction of droplet trajectories in a turbulent flow environment.
3) Experimental research at the Air Pollution Technology Branch of the US Environmental Protection Agency, to investigate the process in turbulent flows.
4) Experimental research at the University of Illinois focuses on design, construction, and application of a laser based LIBS system for measuring droplet size, metal concentration in the gas phase, and metal concentration in the vapor phase. This analysis procedure will be used both at the University Of Arizona laminar flow reactor and the EPA turbulent flow reactor.
5) Theoretical research at the University of Illinois to provide input into the drag model to be used to predict droplet trajectories in hot turbulent flows.

Research Progress and Implications

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

Experiments were performed in the 18 kW laminar downflow furnace at the University Of Arizona. Aqueous solutions the metals were atomized and injected into the flame. Powdered sorbents were injected into the post-flame region of the furnace. Particles were sampled from the furnace isokinetically and passed through a Berner low-pressure impactor. The samples were then analyzed. Extents of reaction for cesium (a semi-volatile metal) were determined through the method of aerosol size fractionation, whereby the fraction of a metal falling in the sub-micron particle size fraction range is considered to be unreacted. Reaction extents of the less volatile strontium were also inferred through the resulting strontium particle size distribution (psd).

Without chlorine or sulfur present, strontium shows a broad peak in the exhaust psd, indicating that the strontium fails to vaporize. Addition of the sorbents creates a sharper peak, but this is probably due to coagulation of the strontium compound onto the sorbent, since the strontium does not vaporize. The experimental evidence suggests that sulfur allows the strontium to vaporize and then nucleate to form small particles, which is different from the equilibrium predictions. However, this enhanced vaporization does not appear to enhance the capture of strontium. Chlorine, however, acts to reduce the dewpoint of strontium. Thus, the metal is in the vapor form (as shown on Fig 1 by the psd around 0.1mm, without sorbent present) over appreciable contact times with the sorbent. In the presence of chlorine, kaolinite can reactively capture strontium as shown in Fig 1 by the shift in the strontium psd to match the sorbent psd. Lime, however, does not capture strontium.

The psd of cesium alone forms a peak at 0.2 mm. This indicates that the cesium volatilizes, and then nucleates in the probe to form a fume of smaller particles. When kaolinite is added, the cesium peak shifts to match that of the kaolinite. This shows that the cesium is reacting with the kaolinite and is scavenged. Lime shows only a minimal amount of capture. When chlorine is added to the system, cesium is still captured onto kaolinite, but not on lime. Sulfur produces a double peak in the distribution curve. In the presence of both sorbents, this appears to enhance the capture.

The significance of these results lies in that they show that high temperatures can be exploited to reactively capture both cesium and strontium on substrates, which can be captured, and effectively isolated from the environment. This is contrary to the conventional wisdom that high temperature processes have no application to the isolation of metal containing radioactive wastes.

Installation of laser diagnostics at the Arizona facility is progressing. Components are being fabricated at the University of Illinois at Urbana-Champaign as outlined in the original proposal, and both the gated CCD and excimer laser have been received and found to meet specifications. Transfer of major equipment items from Urbana to Tucson is anticipated for late summer. Optical engineering is effectively complete, following a site visit by Scheeline and Pearlstein in late May.

A key part of this effort is a model representing a liquid droplet of metal containing hazardous waste transversing a highly turbulent combustor. Even though the combustion of liquid fuels in most practical combustors is not dominated by the trajectory of individual droplets, this knowledge is necessary here in order to predict both the complete vaporization of all the hazardous waste containing drops and the optimum placement downstream of the flame of the injected sorbent to take advantage of the availability, and therefore optimize the capture of the metal vapor. The success of such a model would therefore allow the use of the kinetic data gathered from the University of Arizona's laminar flow reactor to predict and help design larger turbulent flow reactors.

A One Dimensional Turbulence model, devised by Kerstein at Sandia Laboratories, forms the basis on which a computer program describing individual droplet trajectories in turbulent flows has been written and is currently being tested. The purpose of this model is to predict the range of droplet burnout points in the EPA turbulent flow reactor, as measured previously. This program will form the basis for future predictions.

Research at University of Illinois has focused on drag prediction. We have developed a technique for efficiently computing two-dimensional, axisymmetric, or three-dimensional bluff-body wake flows on unbounded domains. The approach makes use of the fact that the vorticity is largely confined to a relatively small subdomian that is either parabolic (for two-dimensional flows) or paraboloidal (in the axisymmetric or three-dimensional cases). We then solve the full Navier-Stokes equations on this domain, subject to the condition that the solution matches the far-field analytical solution of the inviscid equations on the parabolic or paraboloidal boundary. The technique is being demonstrated for rigid bluff bodies (circular cylinders and spheres), and will then be implemented in the drop flows of interest.

Planned Activities

The laser diagnostic system will be applied to the Arizona reactor before December 99, and to the EPA turbulent reactor before July 00. The droplet trajectory model will be calibrated against literature data by October, 99. Several papers on interim results obtained to date are being prepared for publication this year.

A Novel Energy-Efficient Plasma Chemical Process for the Destruction of Volatile Toxic Compounds

Project ID: 54973

Lal A. Pinnaduwage, Oak Ridge National Laboratory

Research Objective

The objective is to develop a novel plasma chemical process for the destruction of low-concentrations (below several percent) of toxic volatile compounds from contaminated air streams. Such contaminated air streams are encountered in air stripping of highly-contaminated water and soil, and also in the incineration of combustible hazardous wastes. Our technique is based on the efficient dissociation of molecules via enhanced electron attachment to highly-excited states of the molecules produced in a glow discharge.

Research Progress and Implications

This project was based on enhanced electron attachment to highly-excited states of molecules observed in laser excited molecules. The basic idea was to achieve molecular excitation using a glow discharge. We have conducted basic studies to illustrate that enhanced electron attachment to highly-excited states can be achieved using both continuous (Refs. JP1,JP3, JP7) and pulsed discharges (Refs. JP2,JP10, JP12). A discharge reactor was constructed and analytical methods were developed to measure the destruction efficiency (Ref. JP8). Plasma remediation experiments were conducted using both continuous (Refs. JP4) and pulsed (Refs. JP11,JP14) discharges using inert gases as the carrier. Furthermore, basic studies were conducted (Refs. JP5,JP6, JP7, JP9, JP12, JP13) in order to clarify the destruction efficiencies observed in the reactor. These studies confirmed our basic idea, and also led to a serendipitous outcome, i.e., the reactor output was free of hazardous gaseous byproducts. In our studies on benzene and methylene chloride, dust particles were observed to accumulate in the reactor. We have conducted several studies to characterize the dust particles produced in a benzene discharge, and they were identified as carbon nanoparticles.

Planned Activities

If the project is to be continued, we plan the following main activities:

1. We propose to test whether the same destruction characteristics hold for other toxic compounds of interest to DOE such as trichloroethylene, carbon tetrachloride, and dioxin.
2. Characterize the dust formed from other pollutants (especially chlorinated compounds) to test whether they have any undesirable properties. The production of nanoparticles in the destruction process may also have commercial value.
3. Conduct studies on the above listed toxic gases in mixtures with air, to determine whether the output will be free of hazardous gases, and whether the dust formation still holds. We have already conducted studies in N_2 mixtures which have shown that dust formation still occurred. We propose to add O_2 and water vapor in their representative concentrations to investigate their influence.

Information Access

JP1. L. A. Pinnaduwage, W. Ding, and D. L. McCorkle, "Enhanced Electron Attachment to Highly Excited Molecules Using a Plasma Mixing Scheme" *Appl. Phys. Lett.* **71**, 3634 (1997).

JP2. L. A. Pinnaduwage, "Implications of Electron Attachment to Highly-Excited States in Pulsed Power Discharges", Digest of Technical Papers of the 11th IEEE Pulsed Power Conference, (Eds. G. Cooperstein and I. Vitkovitsky) IEEE Publishing Services, New York, 1997. pp. 1048-1053.

JP3. W. Ding, D. L. McCorkle, and L. A. Pinnaduwage, "Enhanced Negative Ion Formation by Electron Attachment to Highly-Excited Molecules in a Flowing Plasma", *J. Appl. Phys*. **84**, 3051 (1998).

JP4. 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* , **32**, 46 (1999).

JP5. L. A, Pinnaduwage, P. G. Datskos, W. X. Ding, and D. L. McCorkle, "Enhanced Electron Attachment to Highly-Excited States of Molecules: Implications for Plasma Processing Discharges", Proceedings of the 1998 International Congress on Plasma Physics, Ed. By P. Pavlo, pp. 125-128 (1999).

JP6. L. A, Pinnaduwage, W. X. Ding, and D. L. McCorkle, "Enhanced Electron Attachment to Superexcited Rydberg States of Molecular Hydrogen Using a Plasma Mixing Scheme", Proceedings of the 1998 International Congress on Plasma Physics, Ed. By P. Pavlo, pp. 129-132 (1999).

JP7. L. A. Pinnaduwage, W. Ding, D. L. McCorkle, S. H. Lin, A. M. Mebel, and A. Garscadden, "Enhanced Electron Attachment to Rydberg States in Molecular Hydrogen Volume Discharges", *J. Appl. Phys.*, **85**, 7064 (1999).

JP8. C. Y. Ma, D. L. McCorkle, W. Ding, and 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", *J. Chromatography A*, **844,** 217 (1999).

JP9. L. A. Pinnaduwage, C. Tav, D. L. McCorkle, and W. Ding, "Temperature. Dependence of Electron Attachment to Methylene Chloride", *J. Chem. Phys.*, **110**, 9011 (1999).

JP10. W. Ding, L. A. Pinnaduwage, C. Tav, and D. L. McCorkle, "The Role of High Rydberg States in Enhanced O^- Formation in a Pulsed O_2 Discharge", *Plasma Sources Sci. Technol.*. **8,** 384 (1999).

JP11. D. L. McCorkle, W. X. Ding, C. Y. Ma, and L. A. Pinnaduwage, "Dissociation of Benzene in a Pulsed Glow Discharge", *J. Appl. Phys*., **86**, 3550 (1999).

JP12. L. A. Pinnaduwage, W. X. Ding, D. L. McCorkle, and C. Y. Ma, 'Enhanced Electron Attachment to Highly-Excited Molecules and Its Applications in Pulsed Plasmas", Digest of Technical Papers of the 12th IEEE Pulsed Power Conference, IEEE Publishing Services, New York, (in press, 2000).

JP13. C. Tav and L. A. Pinnaduwage, "Enhanced Dissociative Electron Attachment to Laser-Excited Benzene", submitted to *J. Chem. Phys.* (1999).

JP14. D. L. McCorkle, W. X. Ding, and L. A. Pinnaduwage, "Remediation of Benzene in a Pulsed Glow Discharge: Byproduct Analysis and Dust Formation", to be submitted to *J. Appl. Phys.* (2000).

Ion and Molecule Sensors Using Molecular Recognition in Luminescent, Conductive Polymers

Project ID: 55247

Dr. Michael R. Wasielewski, Argonne National Laboratory

Research Objectives

This program integrates three individual, highly interactive projects that will use molecular recognition strategies to develop sensor technology based on luminescent, conductive polymers that contain sites for binding specific molecules or ions in the presence of related molecules or ions. Selective binding of a particular molecule or ion of interest to these polymers will result in a large change in their luminescence and/or conductivity, which can be used to quantitatively sense the presence of the bound molecules or ions. Molecular recognition sites for a variety of toxic metals and organics will be developed. These include transition metals, heavy metals such as lead, uranium, and plutonium, as well as toxic organics, such as chlorinated and nitrated aromatic molecules. Research problems that will be addressed include: 1) designing molecular recognition sites that are highly selective for the ions and/or molecules 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. Each project is designed to carry out an important aspect of sensor development that will be integrated into an overall effort to produce novel sensors for use in the rapid assessment of environmental remediation strategies.

The Development of Cavity Ringdown Spectroscopy as a Sensitive Continuous Emission Monitor for Metals

Project ID: 60070

Dr. George P. Miller, Mississippi State University

Research Objective

The aim of this study is to evaluate cavity ringdown spectroscopy (CRDS) as an ultra-sensitive technique for trace analysis of metals. Potential applications of CRDS meeting the Department of Energy needs include:

Mercury Continuous Emission Monitor
Multi-Metal Emissions Monitor
Radionuclide Detector and Monitor

CRDS is based upon the measurement of the rate of light absorption in a closed optical cavity. A laser pulse is injected into a stable optical cavity through one of the cavity mirrors. This light pulse is trapped between the mirror surfaces and decays exponentially over time at a rate determined by the round trip losses within the cavity. When used for trace analysis, the primary loss mechanisms governing the decay time are mirror reflectivity losses, atomic absorption from the sample, and Rayleigh scattering from air in the cavity. The decay time is given by

$$\tau = \frac{d}{c\left[(1-R) + \alpha l_s + \beta d\right]} \tag{1}$$

where d is the cavity length, R is the reflectivity of the cavity mirrors, α is the familiar Beer's Law absorption coefficient of a sample in the cavity, l_s is the length of the optical path through the sample (i.e., approximately the graphite furnace length), β is the wavelength-dependent Rayleigh scattering attenuation coefficient, and c is the speed of light.

Thus, variations in α caused by changes in the sample concentration are reflected in the ringdown time. As the sample concentration increases (i.e., α increases), the ringdown time decreases yielding an absolute measurement for α. With the use of suitable mirrors, it is possible to achieve thousands of passes through the sample resulting in a significant increase in sensitivity. An additional benefit is that it is not subject to collisional quenching, the branching of fluorescence emission into multiple transitions, and the ability to detect only a fraction of the fluorescence photons that occur in laser-excited atomic fluorescence (LEAFS). One other advantage of the ringdown technique is the ability to use pulsed UV tunable lasers for atomic absorption spectroscopy.

Research Progress and Implications

This report summarizes work 18 months into a 3-year project. Last year's report focused on the initial results using an ICP as the atomization source. While the development of the ICP-CRDS is continuing, the need for repairs of the ICP system permitted us to begin an evaluation of CRDS using a graphite furnace as the atomization source. It is these results that we will focus on in this report. The introduction of the graphite furnace into the cavity requires simply that the furnace be firmly mounted within the cavity and that the laser beam pass through the center of the graphite tube. Introduction of test samples followed standard electrothermal atomization atomic absorption spectroscopy (ETA-AAS) methods.

Mercury and Lead were chosen for the initial study partly because of the need for mercury monitoring within DOE and partly due to the fact that their volatility would present a challenge to the

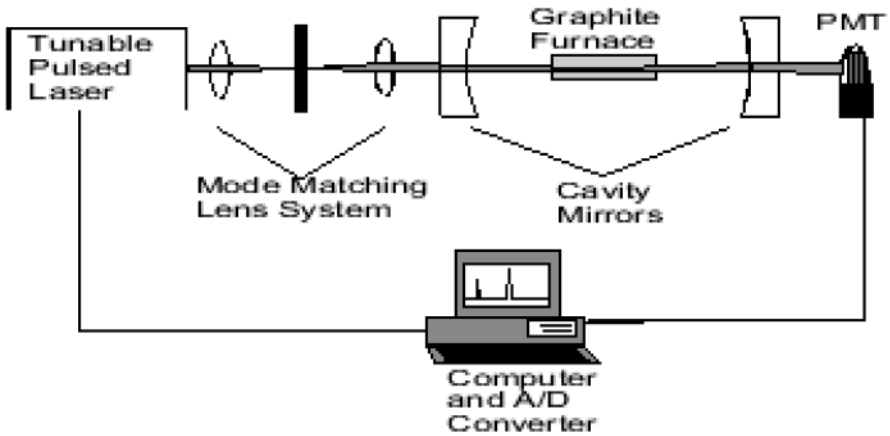


Figure 1: Schematic Diagram of ETA-CRDS System

technique. Preliminary experiments used the Pb 283.3 nm absorption line to confirm the viability of ETA-CRDS for trace analysis. This Pb absorption line was chosen, rather than the stronger 217.0 nm absorption, for convenience with the laser system and cavity mirrors. The Pb solution data for Figure 2 was obtained by injecting 7.5 µl of 2 ng/ml lead standard solution for each heating cycle. As is clear from equation 1, $1/\tau$ is proportional to the absorbance αl_s.

The first experimental data, using ETA-CRDS, indicates that this technique has the potential to significantly enhance the sensitivity of electrothermal atomization systems. Preliminary results for mercury and lead standard solutions gave detection limits of approximately 2.8 and 1 pg respectively were obtained for peak height absorption measurements. No chemical matrix modifiers were used. These detection limits, obtained in a clearly non-optimum experimental setup, compare favorably to commercial GF-AAS systems (Hg DL ~30 pg) that have undergone continuously optimization over many years. Additional experiments to measure a detection limit for Hg using a Hg-hydride cold vapor system as the Hg source are in progress.

Continuing improvement of the ETA-CRDS technique includes optimization of the laser linewidth, cavity stability during the furnace atomization sequence, data acquisition rate and timing, and the operation of the graphite furnace itself. For example, the atomization of lead within the GF is complete in well under one second while the laser repetition rate was only 20 Hz. This implies that the results obtained in this study would greatly benefit from the use of higher repetition rate lasers such as an excimer (100-1000 Hz) or Cu vapor (2-32 kHz) lasers. Finally, in a glance to the future, it is important to note that CRDS has been carried out in other "non-traditional" configurations.

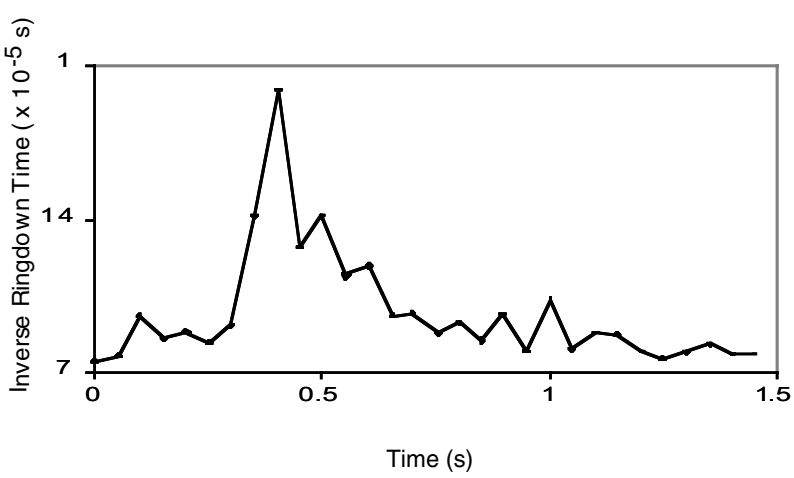


Figure 2: $1/\tau$ (where τ is the ringdown time constant) at 283.3 nm as a function of the data acquisition time following the vaporization of a 7.5 µl of 2 ng/ml Pb solution.

Diode lasers have been employed for CRDS of molecular species at near-infrared wavelengths, and provide a small, compact light source for CRDS measurements. In addition, frequency-doubled diode lasers have been employed at ultraviolet wavelengths for atomic absorption spectrometry (but not CRDS) for a few selected elements. As the wavelength coverage offered by diode lasers and solid state lasers in general continues to grow, the possibilities for constructing small, ultra-sensitive CRDS spectrometers for analytical atomic spectrometry continue to increase

Planned Activities

It is our intention to return our focus to the ICP-CRDS system. Work on optimizing the ICP-CRDS cavity design will be completed within the next couple of months. Several new ICP torches, designed and built to increase sample path and maximize atomization, will also be evaluated and detection limits for various metals established. In addition, the potential for this technique to detect and monitor transuranic elements will be evaluated. With respect to the GF-CRDS, future research will investigate elements of lower volatility and reduced fluorescence yield (such as the actinides), where the advantages of ETA-CRDS (at this stage of technology development) and the needs of DOE are most evident

Information Access

G. P. Miller and C. B. Winstead, Cavity Ringdown Laser Absorption Spectroscopy. Encyclopedia of Analytical Chemistry. Editor R. A. Meyers, John Wiley & Sons Ltd. In preparation.

C. B. Winstead, F. J. Mazzotti, J. Mierzwa, and G. P. Miller, Preliminary Results For Electrothermal Atomization - Cavity Ringdown Spectroscopy (ETA-CRDS). *Anal. Comm*. Accepted.

G. P. Miller and C. B. Winstead, Inductively Coupled Plasma Cavity Ringdown Spectroscopy, *J. Anal. Atomic Spectro.* 12, 907 (1997).

G. P. Miller and C. B. Winstead. ICP-Cavity Ringdown Spectroscopy. Abstract 407, The 25th FACSS Conf. Austin TX 12-15 Oct 1998.

G. P. Miller and C. B. Winstead. ICP-Cavity Ringdown Spectroscopy. Abstract O1-4, Winter Conference in Spectrochemistry. Gent Belgium 12-17th Jan 1997.

Web Site http://www.msstate.edu/dept/dial/1-pg-pdf/icp-crs-0397.pdf

High Fluence Neutron Source for Nondestructive Characterization of Nuclear Waste

Project ID: 54751

Mark M. Pickrell, Los Alamos National Laboratory

Research Objectives

We are addressing the need to measure nuclear wastes, residues, and spent fuel in order to process these for final disposition. At present, no nondestructive assay (NDA) instrumentation is capable of satisfying all of the PDP test cycles (particularly for Remote-Handled TRU waste). One of the primary methods for waste assay is by active neutron interrogation. The objective of this project is to improve the capability of all active neutron system's 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.

Research Progress

This high intensity neutron source is an electrostatically confined (IEC plasma device. Previous experiments[1] have demonstrated a neutron yield of 2 x 10^{10} neutrons/second on a table-top device that can be powered from ordinary laboratory circuits (9 kilowatts). We have established theoretically the basis for scaling the output up to 1 x 10^{11} neutrons / second. In addition, IEC devices have run for cumulative times approaching 10,000 hours, which is essential for practical application to NDA. They have been operated in pulsed and continuous mode.

Most previous IECs have been single grid systems that operate at high density. These systems require high density for breakdown, but this results in a highly collisional plasma which seriously degrades the performance. The novel approach we have implemented at Los Alamos removes this limitation. The Los Alamos IEC uses a triple grid design which uses dispenser cathodes to initiate plasma ionization. We have successfully demonstrated this low density operating regime in the device.

Research Progress and Implications

We also have designed the machine with a capability to go to signicantly higher power levels than previous devices. We have a 75 kV 335 (25kW) milliampere power supply which will significantly push the operation envelope for IECs. This increased power level requires us to actively cool the device. The chamber is a double-jacketed design which is water cooled and the inner grid is made of surgical tubing which is cooled with compressed air.

Typical results to date have been 1.0e6 neutrons per second operating at 40kV and 30 milliamperes of current. We anticipate going to significantly higher currents when we install 6 new dispenser cathodes. Operating at higher voltages will require some modifications to the high voltage grid system. When these modifications are made, we will test operating at maximum power. We will also then have a large enough voltage/current/pressure operating window to test the empirical scaling laws in new plasma regimes.

When we have achieved these parameters in D-D we will then be ready for D-T operation. This will require a hermetically sealed system with a Tritium gettering system to handle the gas.

The major impact of a neutron source of the type we have developed is to cut the time and increase the throughput for nuclear assay of nuclear waste. Potential applications are both for TRU-waste and spent fuel. This technology will help make nuclear assay of waste faster and cheaper. This source potentially has a wide range of applications beyond waste assay that will benefit from real-time assay capability. Other potential applications include landmine detection, high explosive detection, drug detection, SNM detection (nonproliferation), and possibly (in a scaled up version)

radioisotope production and neutron tomography. The neutron source we have built is the first actively cooled IEC source constructed. Our double-jacketed design has been incorporated by NASA into a device being constructed at the Marshall space center and it is being considered by groups the University of Illinois, the University of Wisconsin, and Kyoto University. This project has also been a catalyst for new ideas, including one to develop a similar device for fusion power applications. A project incorporating this idea is presently under construction at LANL and is being funded by the DOE Office of Fusion Energy Science. The primary remaining hurdle at present is simultaneous operation at high voltage and high current. Gas handling technologies also need to be included for D-T operation.

Adsorption/Membrane Filtration as a Contaminant Concentration and Separation Process for Mixed Wastes and Tank Wastes

Project ID: 55146

Dr. Mark M. Benjamin, University of Washington

Research Objectives

The Hanford Reservation is the largest and perhaps most complex Superfund site in the U.S., containing numerous hazardous chemicals and medium- to long-lived radionuclides. Each category of waste presents a different set of scientific and technological challenges for characterization, handling, treatment, storage and disposal. This research is on novel approaches for separating colloidal matter, U, Sr, and Cs from the remaining constituents of the liquid wastes with which they are associated, and from one another.

A wide variety of organic membranes, anion- and cation-exchange resins, other organic adsorbents, solvents and complexing agents have been developed for the treatment of complex, mixed wastes *[IAEA, Advances in technologies, 1994].* Some of the adsorbents and ion-exchange resins are exceptionally selective and efficient, but they have serious drawbacks that impair their performance when used to treat radioactive wastes. Namely, they are susceptible to thermal, chemical (i.e., oxidative), and radiation-induced degradation, and they are often very expensive. The regeneration of organic media with adsorbed or otherwise retained radionuclides often is incomplete, and, given their chemical instability, their safe disposal is an additional problem.

The major focus of this research is the development of advanced inorganic processes to treat radionuclide-bearing wastes. Inorganic materials are generally much cheaper and less prone to deterioration in radioactive environments than organic materials, their long-term behavior is easier to predict, and they can be used in vitrification processes. However, for inorganic materials to be useful in such applications, significant improvements are needed in their mechanical properties, adsorption and/or exchange capacity, and level of characterization. In this proposal, we explore new processes that employ relatively inexpensive and easy-to-use inorganic materials specifically designed to satisfy the needs of mixed nuclear waste treatment. Another major, novel aspect of this research is the combination of inorganic media with electrochemical methods to enhance, accelerate or create an additional useful control parameter in treatment process.

Proposed Separation Process

Many Hanford wastes contain radionuclides, heavy metals, organic solvents, complexing agents, and inorganic salts (predominantly NaOH and $NaNO_3$) *[Gephardt and Lundgren; Tank Farm Surveillance, 1993; Chaiko, Vojta, and Takeuchi 1995].* The sequential treatment system which we propose to develop has as its ultimate goal the separation of contaminants into sub-groups which subsequently can be processed and disposed of appropriately, depending on their properties and the risk they pose. The major emphasis of this research is on the treatment of low-organic waste. Many of the organic contaminants that might be in the waste are unlikely to interfere with process performance. On the other hand, additional treatment steps might be required to eliminate or deactivate some such species (e.g., complexing agents that are present in significant concentrations).

Research on those portions of an overall treatment process is not included in the proposed effort.

Although the speciation of each contaminant depends on the particular waste being treated, most of the waste is alkaline or neutral *[Gephardt and Lundgren].* Therefore, we anticipate that many of the contaminants of concern (actinides, some other radionuclides, heavy metals) are primarily

associated with solids, either as mixed, bulk solids or adsorbed on other particulate matter. The solids range in size from microcolloids to large, settleable particulates. The microcolloids pose major problems for many types of solid/liquid separation systems, since they do not settle easily and can clog filtration systems (either granular media or membrane filters). The first research task will focus on acquiring a more complete understanding of the functioning of an advanced membrane filtration (AMF) system that our group has been developing and that shows promise as an efficient process for removing particulate matter from aqueous wastes. We also propose to study a process developed by other researchers for minimizing fouling of membranes known as electrically enhanced filtration (EEF), and to evaluate a unique combination of these two new technologies.

Novel Miniature Spectrometer for Remote Chemical Detection

Project ID: 60231

Dr. Andrew C. R. Pipino, National Institute of Standards and Technology (NIST)

Research Objective

To develop a new optical technology for chemical detection that is highly sensitive, miniature, rugged, and permits remote sensing of hazardous gaseous, liquid, or semi-solid environments.

Research Progress and Implications

This report, which summarizes work completed as of year 2.4 of a three year project, describes a novel chemical sensing technology that extends cavity ring-down spectroscopy (CRDS) to condensed phases. Applied mostly to gas-phase diagnostics previously, CRDS is an optical absorption technique that uses the photon intensity decay time or "ring-down" time of a low-loss optical cavity as the absorption-sensitive observable. Yet by employing intra-cavity total-internal-reflection (TIR) with monolithic, miniature, optical resonators, a novel variant of CRDS is achieved. TIR provides effective mirror reflectivities of R~0.999999 and generates an evanescent wave with an enhanced electric field at the TIR interface that permits absorption of an ambient condensed phase to be probed. Evanescent wave cavity ring-down spectroscopy (EW-CRDS) combines the advantages of evanescent wave spectroscopy with CRDS.

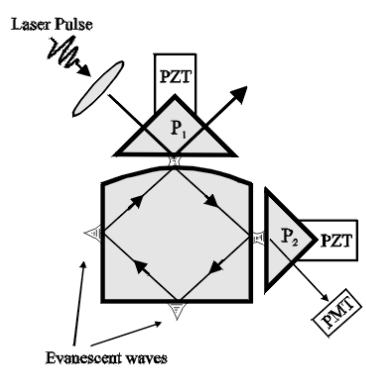


Figure 1: TIR-ring cavity

Several cavity designs for applying EW-CRDS have been realized. In Figure 1, a square, TIR-ring cavity is depicted with a convex facet that refocusses the internally circulating light beam. This cavity is an example of a more general class of polygonal TIR-ring resonators, which was explored theoretically in detail during the initial phase of this work[1]. The round-trip optical loss, L_0, can be made very small ($10^{-3} < L_0 < 10^{-7}$) by using ultra-pure optical materials, ultra-smooth surfaces, and optimized coupling. Photon tunneling across the junctions between the monolithic cavity and the coupling prisms P_1 and P_2 is used for input and output coupling, respectively. Evanescent waves emanate from the remaining facets to probe the absorption of an ambient medium. Figure 2a shows single-shot ring-down traces with decay times of 1.270 µs and 1.278 µs for s- and p-polarized cavity modes, respectively, obtained at 580 nm for a 7 mm x 7 mm x 5 mm fused-silica cavity with a 2.23 cm radius of curvature convex facet[2]. The inset in Figure 2a defines the surface coordinate system and shows the components of the electric field intensity of the evanescent wave as a function of

distance from the cavity facet. With knowledge of the field magnitude and direction, measurement of the ratio of s- to p-polarized absorptions can be related to the molecular orientation. Figure 2b shows ring-down traces for s- and p-polarized modes under identical conditions with Figure 2a, but a TIR facet has been exposed to I_2 vapor, which has a visible X-B transition dipole moment that is aligned with the molecular axis. Note that both s- and p-polarized modes show a change in ring-down time with τ_s=0.497 μs and τ_p=0.889 μs, but the s-polarized mode shows a significantly larger change, despite the smaller field enhancement associated with E_y, indicating that I_2 molecules are preferentially oriented with their molecular axes parallel to the surface. The measurement of molecular orientation is important for chemical sensing because molecules often have a preferential orientation on a surface and because oriented molecular films can be combined with EW-CRDS to increase selectivity. The estimated minimum coverage for detecting adsorbed I_2 is 0.006 % of a monolayer for this prototype, which is instrumentation-limited in these results. Improvements in sensitivity can be anticipated by reaching the shot-noise limit at high fluence and by further reducing round-trip cavity loss. The square fused silica cavity of Figure 1 permits adsorbed vapors to be probed from the near-UV through the near-IR spectral regions. A hexagonal, sapphire TIR-ring cavity has also been successfully fabricated and tested that allows liquid samples to be probed by direct immersion.

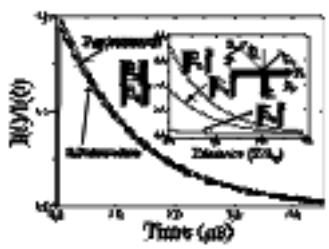


Figure 2a. No adsorbed I_2

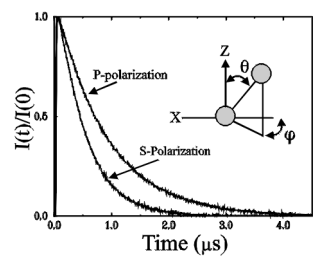


Figure 2b: w/adsorbed I_2

Since the TIR-ring cavity uses only TIR mirrors, a broad spectral bandwidth is accessible. However, photon tunneling is needed to excite and detect the cavity modes, which requires precise positioning of the coupling prisms. Another monolithic resonator design for EW-CRDS is shown in Figure 3 that employs both ultra-high reflective coatings and TIR[3]. Although a restricted bandwidth (~80 nm) results from the use of reflective coatings, this resonator provides high-sensitivity, excellent stability, and facile operation for single wavelength monitoring applications. Light is injected into the cavity through one of the coated facets, along the folded optic axis. The single convex TIR surface imparts stability (refocussing) and generates an evanescent wave. Figure 4 demonstrates the detection of iodine at 530 nm with a fused-silica resonator having an unfolded cavity length of L=3.0±0.1cm, a radius of curvature R_C=7.5±0.1 cm, and Θ_i =45.0°±0.08°, which employs an ultra-high-reflective coating centered at ~520 nm with an estimated loss of L_C=1.2x10^{-5} per reflection. An excimer-pumped dye laser was used without mode matching as the laser source. The transmission through surface S_3 was monitored with a photomultiplier tube and an 8-bit digital oscilloscope. The time dependence of the signal arises from the slow reaction of I_2 with adsorbed water and surface hydroxyl groups. The sensing surface can be easily interfaced to a sample chamber by O-ring seal, as indicated in the inset a of Figure 4.

In order to develop a portable, inexpensive sensing technology based on EW-CRDS, the use of diode laser sources has been examined in collaboration with our commercial partner. In order to obtain the best possible ring-down time measurement precision, which optimizes sensitivity, single mode excitation is required. Furthermore, the laser diode must be optically isolated from the cavity to prevent optical feedback, which shifts and distorts the diode output, rendering single mode matching impossible. Having resolved these issues, we are now able to achieve extremely efficient (58:1), single, lowest-order mode (TEM_{00}), excitation of CRDS cavities with a standard, off-the-shelf diode laser (not an extended cavity diode laser system). These experiments used a 685 nm diode with a 15±5 MHz linewidth, which provided ample cavity output intensity (~10 μW) for detection. These results indicate that a cost effective sensing system based on EW-CRDS can be produced. Furthermore,

the sensing element (the resonator) can be remotely located from the source and detector by optical fiber or all three miniature elements could be packaged on a chip.

Finally, we are examining the combination of "smart films", which show molecular recognition for a particular molecule or class of molecules, with EW-CRDS. Working with collaborators at LANL, we have tested cyclodextrin films which show selectivity for toluene. Initial results indicate that these films, which form rugged, well-ordered monolayers on superpolished surfaces, show low-scatter loss and low total attenuation. Therefore, functionalizing the surfaces of EW-CRDS resonators to increase selectivity should be feasible.

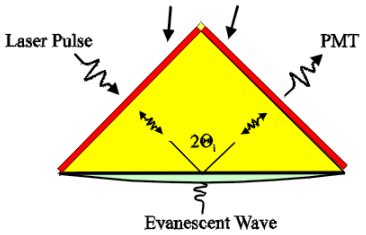


Figure 3: Folded, monolithic cavity

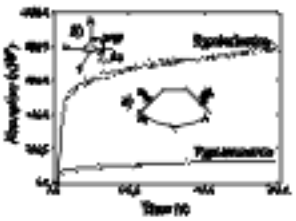


Figure 4: I_2 detection

Planned Activities

During the remaining months of FY 2000, we anticipate continuing our investigation of the combination of EW-CRDS with smart films. We will also employ diode laser excitation with several EW-CRDS cavity designs. Experiments on bulk liquids will also be explored.

Information Access

1) A. C. R. Pipino, et al. Rev. Sci. Instrum. **68** (8), 2978-2989, (1997).
2) A. C. R. Pipino, Phys. Rev. Lett. **83** (15), 3093-3096, (1999).
3) A. C. R. Pipino, Appl. Opt. March 20, 2000.
4) Also see patents: US5835231, US5943136, US5986768

Development of Advanced In Situ Techniques for Chemistry Monitoring and Corrosion Mitigation in SCWO Environments

Project ID: 55171

D. D. MacDonald, The Pennsylvania State University

S. N. Lvov, The Pennsylvania State University
X. Y. Zhou, The Pennsylvania State University
X. Wei, The Pennsylvania State University
S. M. Ulyanov, The Pennsylvania State University

Research Objective

Super Critical Water Oxidation (SCWO) is a promising technology for destroying highly toxic organic waste (including physiological agents) and for reducing the volume of DOE's low-level nuclear waste. A major problem inhibiting the wide implementation of SCWO is the lack of fundamental knowledge about various physico-chemical and corrosion processes that occur in SCW environments. In particular, the lack of experimental techniques for accurately monitoring important parameters, such as pH, corrosion potential, and corrosion rate, has severely hampered the development of a quantitative understanding of the degradation of materials in this extraordinarily aggressive environment. Accordingly, the principal objective of the present program has been to develop new, innovative methods for accurately measuring parameters that characterize corrosion processes under super critical conditions.

Research Progress and Implications

As a result of our three-year effort, we have developed new chemical and corrosion sensors for use in high subcritical and supercritical aqueous environments. In particular, a novel flow-through yttria-stabilized zirconia (YSZ) pH electrode and a flow-through external reference electrode have been developed and evaluated. Potentiometric measurements have been carried out to determine the pH of dilute hydrochloric acid (from 0.001 to 0.01 mol kg^{-1}) at temperatures up to 400°C. High precision potential data were obtained with an uncertainty of ± 3 mV. The association constant of hydrochloric acid was evaluated to judge the accuracy of the pH measuring system. The results have been compared with available literature data and good agreement between experimentally measured and literature data is obtained, demonstrating that quantitative potentiometric studies on aqueous solutions at temperatures above the critical temperature are now possible.

Three-electrode electrochemical noise (EN) sensors have been developed for measuring corrosion rate in subcritical and supercritical environments. The EN sensors were tested in flowing aqueous solutions containing NaCl and HCl at temperatures ranging from 150° to 390°C, at a pressure of 25 MPa, and at flow rates from 0.375 ml/min to 1.00 ml/min. The noise records in the potential and coupling current from Type 304 stainless steel were recorded simultaneously. The inverse noise resistance ($1/R_n=\sigma_I/\sigma_E$) was calculated from the standard deviations in the current (σ_I) and potential (σ_E) and was compared with the corrosion rate determined via mass loss measurements. The inverse noise resistance correlated very well with the measured corrosion rate measured at various temperatures and flow rates. At temperatures higher than 150°C, the corrosion rate was found to be proportional to the inverse noise resistance as required by the Stern-Geary relationship. Accordingly, noise resistance can be used to evaluate corrosion rate in these aggressive, low density (super critical)

environments. Good agreement was found between the Stern-Geary constant evaluated via electrochemical noise analysis (ENA) and that determined via polarization measurements. To our knowledge, the work reported here represents the first determination of corrosion rate using electrochemical noise techniques in super critical aqueous solutions.

A phenomenological model that was previously developed to account for the dependence of corrosion rate of steel in super critical aqueous systems on pressure. The model takes into account the effect of pressure on the volumetric concentration of the reactant (e.g. O_2), the compression of the solvent (water), and the activation process through the finite volume of activation. The model has been used for Stone & Webster Engineering Co. to estimate corrosion rates of materials in the US Army's SCWO program for the destruction of hydrolysate from the chemical agent, VX. In particular, the model was used to correct the corrosion rates measured at MIT for differences in pressure between the laboratory studies and the MOC (Materials of Construction) work that was being carried out at General Atomics in La Jolla, CA.

The current project has been completed and a proposal for follow-on work is currently being prepared.

Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance

Project ID: 54864

Dr. Kristin Bowman-James, University of Kansas

Bruce Moyer, Oak Ridge National Laboratory

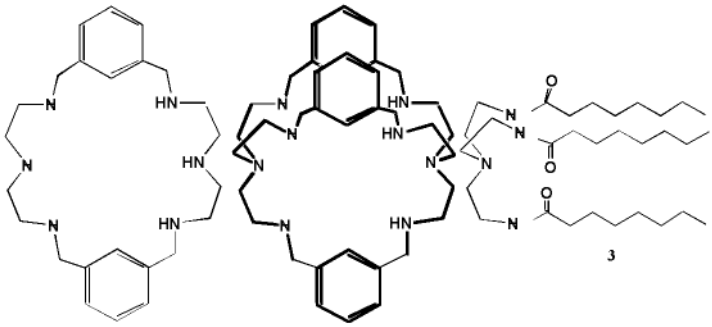
Research Objective

This project had as its original focus the design and synthesis of polyammonium macrocyclic receptors for oxoanions of environmental importance and specifically those found in high level waste tanks. This third year of the project, we have added the goal of synthesizing lipophilic amide-based receptors in order to increase the potential for obtaining workable receptors for both separations and sensing applications. Three areas of emphasis are being explored. Major efforts are being made in the design and synthesis of receptors that exhibit highly selective binding for specified anions. A basic research component inherent in this effort is to devise new and improved synthetic techniques that would allow for obtaining economically feasible receptors. A second effort includes structure determination and thermodynamic studies in order to ascertain structural criteria for anion binding as well as to determine the strength of binding. A third area of thrust is in theory and involves molecular dynamics simulations in order to assess the solution characteristics of the interactions between anions and their receptors. Theoretical studies are being performed in collaboration with Professor Krzysztof Kuczera. Additionally, two applications-oriented efforts are being explored. The fabrication of systems for liquid-liquid separations is being explored in a subcontract with Dr. Bruce Moyer at Oak Ridge National Laboratory. At the University of Kansas, a method known as ITIES (Interface between Two Immiscible Electrolyte Solutions) is being explored as a means to achieve sensors for the *in situ* quantitative determination of a variety of anions in groundwater. This is a collaborative effort with Professor George Wilson.

Research Progress and Implications

This report summarizes work after 2 years and 7 months of a three year project. To date we have focused on the design and synthesis of selective receptors for oxo anions with considerable effort on nitrate.

Synthesis. In year one of the project polyaza macrocycles and macrobicycles were identified which bind the desired anions and are easy to synthesize via two step Schiff base/reduction processes with high yields. During year one most of our studies focused on monocyclic systems, e.g., **1**. In



year two (as a result of findings from molecular dynamics simulations) we began to examine bicyclic macrocycles, e.g., **2**. In year three, in an effort to synthesize receptors which do not have the pH dependence that **1** and **2** have and which have a greater solubility in organic media, we synthesized a series of lipophilic tripodal amides, e.g., **3**.

Structural studies. A number of crystal structures have now been obtained for anion complexes including nitrate, sulfate, phosphate, chloride, and fluoride. While the monocycles rarely bind the anions inside the ring, we have several structures of bicyclic complexes with anions inside the cavity. These include a "dinitrate" complex and a fluoride complex in which both fluoride and water are in the cavity, both with receptor **2**. With respect to the dinitrate structure, this exciting result indicates that these bicycles hold considerable promise as receptors for trigonal anions. To our knowledge this is the first example of a receptor incorporating two discrete anions within a single cavity. Another unique crystal structure of **3** with nitrate shows the formation of bilayers with channels holding the nitrate ions. Very few crystal structures have been reported with lipophilic species such as ours.

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. MD studies have also indicated that water plays an important role in solution, in forming relay networks to the macrocyclic receptor from surrounding nitrates.

Potentiometric studies. Protonation and binding constants were determined for monocycles and bicycles using potassium *p*-toluenesulfonate as electrolyte, based on the assumption that the *p*-toluenesulfonate anion is sufficiently large to exhibit negligible binding affinity and thus does not compete with the anions under investigation. The results of the potentiometric studies indicate that for monocycles, association constants are lower than the bicycles (K_{as} *ca.* 10-100) with the exception of sulfate (dinegative charge enhances binding). This finding is undoubtedly due to the interfering or competing influence of hydration on anion binding, as noted in the molecular dynamics studies during the first year of the grant. However, affinities of the bicyclic receptors for nitrate are all considerably larger with K_{as} ranging from $10^3 - 10^5$. Binding studies have also been performed for the lipophilic receptors such as **3** and indicate as anticipated that affinities are somewhat lower than for the polyammonium bicycles. Affinities for the amides are about the same order of magnitude as the monocycles.

Separations studies. (Subcontract with Bruce Moyer at Oak Ridge National Laboratory) Studies at Oak Ridge began last summer. Using the lipophilic receptors (**3**) Moyer found that extraction of $CsNO_3$ was enhanced when a dual receptor system (the lipophilic amide in conjunction with a crown ether) was used. These results are very exciting and perhaps represent the first example of the use of a dual receptor in separations technology.

Planned Activities

This is the last year of the project. We are finishing titrations of the polyammonium and lipophilic amide receptors. The most promising aspects of earlier findings are being pursued further (and will provide the preliminary data for new proposals). These aspects include the bicycles capable of incorporating multiple anions, the new lipophilic receptors, and the dual receptor systems for cation-anion pairs in both separations and sensors.

Information Access

The structure of the nitrate complex of **2** may be viewed at the following web site: http://129.237.102.17/~kuczera/kristin/animate.html.

Publications

S. Mason, T. Clifford, L. Seib, K. Kuczera, and K. Bowman-James, Unusual Encapsulation of Two Nitrates in a Single Bicyclic Cage, *J. Am. Chem. Soc.* **1998**, *120*, 8899-8900.

C&E News concentrate. September 7, 1998, page 30, "Two nitrates in a cage."

J. Wiórkiewicz-Kuczera, K. Kuczera, C. Bazzicalupi, A. Bencini, B. Valtancoli, A. Bianchi, and K. Bowman-James, Solid State to Solution: Crystal Structure and Molecular Dynamics Simulations of a Polyammonium Nitrate Host, *New J. Chem.*, accepted pending revision.

T. Clifford, L. Seib, K. Bowman-James, Fluoride and Water, Co-habiting Guests in a Bicyclic Host, submitted to *Angew. Chem.*

Invited Lectures

American Chemical Society, Boston. August 25, 1998. Daryle Busch Symposium: Supramolecular Chemistry of Anions

XXIV International Symposium on Macrocyclic Chemistry, Bellaterra (Barcelona) July 18-23, 1999, Plenary Lecture: Supramolecular Chemistry of Anions and Macrocycles

Books and Chapters

Supramolecular Chemistry of Anions, A. Bianchi, K. Bowman-James, E. García-Espana, Eds. Wiley-VCH: New York, 1997, 461 pp.

J. Wiórkiewicz-Kuczera and K. Bowman-James, Anion Binding Receptors: Theoretical Studies, in *Supramolecular Chemistry of Anions*, A. Bianchi, K. Bowman-James, E. García-España, Eds.; Wiley-VCH, New York, 1997, pp. 335-354

Real-Time Broad Spectrum Characterization of Hazardous Mixed Waste by Membrane Introduction Mass Spectrometry

Project ID: 59981

Charles W. Wilkerson, Jr., Los Alamos National Laboratory

Research Objective

The goal of this project is to expand the range of chemical species that may be detected by membrane introduction mass spectrometry (MIMS) in environmental monitoring applications. The driving force is the need for a rapid, sensitive, and broadly applicable tool for characterizing organic and metal-containing contaminants in a variety of DOE (and other) waste streams.

Research Progress and Implications

This section summarizes work completed over the first 30 months of the 3-year program. There are four areas of research and development that we have been engaged in to extend our current level of expertise to a broad analytical methodology: (1) novel ionization techniques, (2) extension of MIMS to environmentally significant volatile (VOC), semi-volatile (SVOC), and metal-containing compounds in air and water, (3) simultaneous detection of VOC, SVOC, and organometallic compounds in air or water matrices, and (4) application of tailored membranes for selective measurement of specific classes of hazardous chemicals.

Novel Ionization Methods. Charge exchange ionization in conjunction with MIMS provides a sensitive method for detecting compounds in air and/or water, and is simple to implement. While the polymer membrane acts as a semi-permeable barrier between a sample and the vacuum of the mass spectrometer, the overwhelming prevalence of oxygen and water in air and liquid matrices, respectively, leads inevitably to the permeation of these species through the membrane. We have turned this potential liability into a significant advantage by exploiting the ability of the ion trap mass spectrometer to perform controlled gas phase chemistry. The water or oxygen is used to generate chemical reagent ions that enhance analyte signals anywhere from 2 to 20 times over those obtained from more traditional electron impact ionization, with a concomitant reduction in detection limits. In the second year of the project, significant effort was directed towards the development of a microwave induced plasma (MIP) ionization source interfaced with MIMS. The motivation for this work was the fact that such discharge ionization techniques are often very efficient (up to 5%), which would further reduce the method detection limit. Initial measurements of rare gases using a directly coupled MIP/ion trap mass spectrometer system (i.e. with no membrane introduction) were promising, however sensitivity to environmentally important compounds was not as good as initially anticipated. Flow injection measurements using various analytes (ferrocene, triphenyltin chloride and aniline) showed distinct changes in the color of the plasma discharge, but little ion signal was observed in the mass spectrometer. Detailed modeling of the instrument using the SIMION ion optics simulation package and extensive experiments suggest that the lack of ion signal is due to poor ion transmission from the plasma discharge source to the ion trap mass spectrometer. Further work would be required to achieve the performance necessary for environmental characterization applications. We believe that chemical ionization (as described above) will provide outstanding detectability for our analytes of interest, and consequently there are no plans to pursue further MIP/MIMS experiments.

Environmentally Significant Compounds. The contamination of air and/or drinking and ground water by organic compounds and heavy metals is a major environmental problem and concern. Over

the course of this project we have successfully demonstrated the real-time detection of (1) methanol, a problematic analyte for GC techniques (due to its high solubility in water), in air and water using MIMS; (2) several semi-volatile compounds (e.g. dimethyl methyl phosphonate, malathion, nitrobenzene, methyl salicylate, 2-chlorophenol, cyclohexanol, diethyl malonate, and naphthalene) in air; (3) metal-containing compounds (ferrocene, $(^5\text{-}C_5H_5)_2Fe$, and molybdenum hexacarbonyl) in air; and (4) a wide variety of volatile organic compounds in air. We have also investigated the transport of various substituted phenols through PDMS (polydimethylsiloxane) membranes in order to gain a better understanding about the mechanism of compound permeation (i.e. solubility and diffusivity) and detection. The time from sample introduction to both initial ion signal and steady-state response depends primarily on the membrane interaction with each compound, and secondarily on the ion trap mass spectrometer response (i.e. ionization efficiency) to each compound. Using oxygen charge exchange ionization, we have observed that flux is enhanced for phenols with electron donating (such as $-CH_3$) versus electron withdrawing (such as –Cl) substituents. For example, 2,4-dimethylphenol diffuses more readily (the initial response time is 1.5 times faster) through the membrane than 2,4-dichlorophenol. Further, other metal-containing compounds (in addition to the iron and molybdenum species mentioned above), such as lead acetylacetonate ($Pb(acac)_2$) and $Ni(acac)_2$, have also been investigated. Using either charge exchange or electron impact ionization, we were able to detect the acac ligand, but not the metal ion nor the intact molecular ion for these two species. To date, we have not used derivatization chemistry to enhance permeation and/or ionization, however, this is an area that needs further exploration.

Simultaneous Detection. We have further demonstrated the versatility of MIMS for the simultaneous detection of VOC, SVOC, and organometallic compounds in air and water using charge exchange (CE) ionization. As mentioned above, CE ionization produces enhanced molecular ion signal over electron impact ionization (EI). This is a result of the fact that more internal energy is deposited to the molecule in the EI process, leading to more fragmentation of the analyte than by CE with $O_2^{+?}$ or H_3O^+. When mixtures of compounds are analyzed, quantification may be more easily accomplished with CE ionization where fewer ions resulting from fragmentation are observed or only the molecular ion is detected. These results are promising for the eventual implementation of a near real-time method for mixed waste characterization at a number of the DOE sites that can lead to substantial savings in time and costs.

Recent Results. During FY00 we have been conducting experiments aimed at tuning the selectivity of pervaporation membranes in order to optimize the measurement of specific classes of hazardous chemicals. Silicone (PDMS) membranes are well-suited for real-time analysis of non-polar and moderately polar volatile organic compounds. However, analyses of more polar and less volatile analytes are often more difficult with a silicone membrane, because of decreased solubility and diffusivity issues. In collaboration with R. B. Timmons (Dept. of Chemistry, University of Texas at Arlington), we are developing new membranes with tunable properties that will allow us to largely avoid such problems. Both the nature of the monomer (e.g. dimethylsiloxane, allyl alcohol, methylamine, etc.) and the conditions under which it is polymerized (pressure, plasma duty cycle, final film thickness) can be controlled to achieve desired membrane performance. Preliminary data show that, compared to a PDMS membrane, a particular plasma-deposited allyl alcohol membrane enhances the detection of polar organic compounds while simultaneously suppressing the detection of non-polar species. By simply changing the plasma duty cycle during polymerization, this same monomer produces a membrane with completely reversed MIMS properties (i.e. suppression of polar, and transmission of non-polar, analytes). We feel that exploitation of this new paradigm in MIMS will allow the development of a truly broad-spectrum technique.

Planned Activities

For the remainder of the FY, we will be performing experiments using a combination of tailored membranes and chemical ionization strategies to map the extent of analyte physicochemical properties accessible to this technique. We will also investigate the use of serial membranes with different pervaporation characteristics to provide chemical class separation (polar vs. non-polar species),

resulting in additional selectivity at almost no cost to analysis time. We have applied for a renewal of this program in order to fully exploit the almost limitless possibilities available with chemically controlled membranes for environmental applications.

Information Access

Multiple presentations at universities and national meetings (ACS, ASMS, WM99, Pittcon, Arizona St. Univ., Univ. of Texas-Arlington, Univ. of North Dakota); four manuscripts to peer-reviewed publications and/or books (listed below).

1. "Real-time Analysis of Methanol in Air and Water by Membrane Introduction Mass Spectrometry." Allen, TM; Falconer, TM; Cisper, ME; and Wilkerson, CW. Submitted to Analytical Chemistry (JAN 2000).
2. "Membrane Introduction Mass Spectrometry: Trends and Applications." Johnson, RC; Cooks, RG; Allen, TM; Cisper, ME; and Hemberger, PH. Mass Spectrometry Reviews, 2000, 19, 1-37.
3. "Simultaneous Detection of VOCs, SVOCs, and Organometallic Compounds in Air and Water by Membrane Introduction Mass Spectrometry." Allen, TM; Cisper, ME; and Wilkerson, CW. In Preparation for Analytical Chemistry (MAR 2000).
4. "Environmental Monitoring" in Membrane Introduction Mass Spectrometry, Cisper, ME; Allen, TM; Kotiaho, T; Ketola, R.; Editors: R. Graham Cooks and Tapio Kotiaho, J. Wiley & Sons, Inc., Invited book chapter. In Preparation.

Architectural Design Criteria for f-Block Metal Ion Sequestering Agents

Project ID: 54679

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-Berkeley

Research Objective

Critical tasks in the cleanup of U.S. Department of Energy (DOE) sites include processing radioactive wastes for disposal in long-term storage, remediation/restoration of environmental sites resulting from radioactive contamination, and decontamination/ decommissioning of nuclear facilities. Because the radioactive components, most of which are metals, are typically present in very low concentrations, it is desirable to remove them from the bulk of the contaminated source (process waste stream, groundwater, soil) and concentrate them to minimize the volume of radioactive material destined for permanent subsurface disposal and thus minimize disposal costs. As the cleanup problem continues to be defined and regulatory limits continue to decrease, ever-increasing demands will be placed on separation technologies for metallic radionuclides. Another important aspect of the site cleanup is the characterization, detection, and monitoring of radionuclides in mixed waste, ground water, contaminated soils, and process streams. The current technology, which involves collection of samples and subsequent laboratory analysis in a remote location, is extremely time and labor intensive. This drives the widespread need for portable, real-time, in situ metal ion sensors.

Organic ligands, i.e., chelating or sequestering agents, with a high degree of metal ion specificity are essential precursors for the development of both separation processes and sensors for radionuclides. In this context, there is a large group of scientists involved in a global effort to discover new ligands. Much of this work, funded by various nuclear agencies, involves the synthesis of novel organic molecules and the study of their reactivity toward metal ions. The objective is to obtain very high selectivity – the ability to discriminate between the target metal(s) and the other metals that may be present in the matrix. Ligand development is the process of synthetically connecting groups of donor atoms to form multidentate binding sites. The way that the donor atoms are connected, i.e., the architecture of the ligand, can have a dramatic impact on the resulting reactivity and selectivity toward metals. For most types of donor atoms, there is no method to predict these structural effects prior to synthesis. Thus, the current state of the art in ligand development remains largely an Edisonian enterprise, a challenging and labor-intensive process.

The objective of this project is to facilitate the ligand development process for f-block metal ions, i.e., the actinides and lanthanides, by developing an accurate set of criteria for the design of ligand architectures. To achieve this objective we first combine theory and experiment to understand the nature of fundamental interactions in selected metal-ligand systems. These design criteria will provide a basis for proposing improved ligand architectures. We then incorporate this understanding within the framework of a molecular mechanics force field to allow the rapid calculation of geometries and energies for ligands and their metal complexes. This computational model will provide a method for quickly screening proposed architectures to identify the best candidates for subsequent synthesis and testing.

Research Progress and Implications

This report summarizes work after 3 years of a 3-year project. There are a number of donor groups that have a known affinity for the f-block metal ions including amides, phosphine oxides, pyridine N-oxides, and catecholates. To make the best use of our resources, we decided early in the project to focus on only one type of donor group. We selected amides because (1) of the amount of existing experimental data on this class of molecules, (2) the ease of synthesis, (3) the availability of molecular mechanics parameters for amides, and (4) the current interest in amide bearing ligands as actinide extractants, e.g., the TRUEX process (actinide separation process under testing for use in tank waste cleanup at Idaho National Engineering and Environmental Laboratory) and DIAMEX (actinide separation process under development in Europe for treatment of commercial nuclear reprocessing wastes).

Our objective has been achieved with respect to the amide donor group. An accurate set of criteria for the design and evaluation of multi-dentate ligands composed of amide functionality has been developed. Experimental research efforts included the synthesis and characterization of amide ligands and amide-metal complexes as well as the generation of structure-function data through the study of f-block metal ion binding affinities using solvent extraction and solution calorimetry. Theoretical research efforts included the use of electronic structure calculations for the detailed analysis of the shapes and energetics of both amides and their metal complexes. A molecular mechanics model that rapidly predicts the geometries and energetics of amides and their complexes with all metal ions in the Periodic Table, including the actinides and lanthanides, has been developed and validated.

Application of this model has revealed that diamide structures currently used as metal ion sequestering agents in solvent extraction systems, i.e., malonamide derivatives, are poorly organized for chelation. Our results indicate that alternate diamide architectures can yield significant increases in binding affinity for the trivalent actinides. For example, we have identified a novel diamide architecture that is predicted to enhance Am(III) binding affinity by 4 orders-of-magnitude.

Other Access to Information

This project has resulted in 23 peer-reviewed publications either in print, accepted, or submitted. Further details on this research are available in progress reports PNNL-11589, PNNL-11899, and PNNL-12208, and at the EMSP web page http://emsp.em.doe.gov.

Rational Design of Metal Ion Sequestering Agents

Project ID: 60370

Dr. Kenneth N. Raymond, Lawrence Berkeley National Laboratory

Jide Xu, University of California

Research Objectives

This project addresses the fundamental issues and requirements for developing hazardous metal ion separation technologies applicable to the treatment and disposal of radioactive waste. Our research encompasses the following areas: the design and synthesis of metal ion specific sequestering ligands, structural and thermodynamic investigations of these ligand and the complexes formed with targeted metal ions, and the development and incorporation of these ligands into applied separation technologies as highly effective materials for hazardous metal ion decontamination.

Research Progress and Implications

This report summarizes our advances over the last year investigating new catecholate-based ligands for Pu(IV). The metal ions Fe(III), Ce(IV), and Th(IV) are convenient to use as Pu(IV) surrogates because they are all hard Lewis acids with similar charge-to-size ratios. Herein is described the synthesis, thermodynamic studies, and extractant properties of our current chelators.

The ligands currently under investigation, illustrated in Figure 1, are the 2,3-dihydroxyterephthalamides **1** (TAMs) and the 3,4-dihydroxysulfonamides **2** (SFAMs). The acidity of the catecholate protons of PTAM **3** is correlated with a strong affinity for Fe(III).[1] The pM value[2] of 22.8 is higher than for any other bidentate ligand and the overall stability constant[3] of 43.1 is the second highest for any bidentate ligand with Fe(III). In addition, the two amides provide sites for functionalization to suit specific applications.

We have chosen to investigate sulfonamide derivatives as a new class of actinide chelators to take advantage of the excellent chelating properties for highly charged metals. The one bidentate ligand with a higher overall formation constants with Fe(III) is 4,5-dihydroxy-1,3-benzenedisulfonate **4**. The stability constant is 46.3 however the pM value of 20.7 is lower than the TAMs. We can also control the solubility properties through proper functionalization of the sulfonamides.

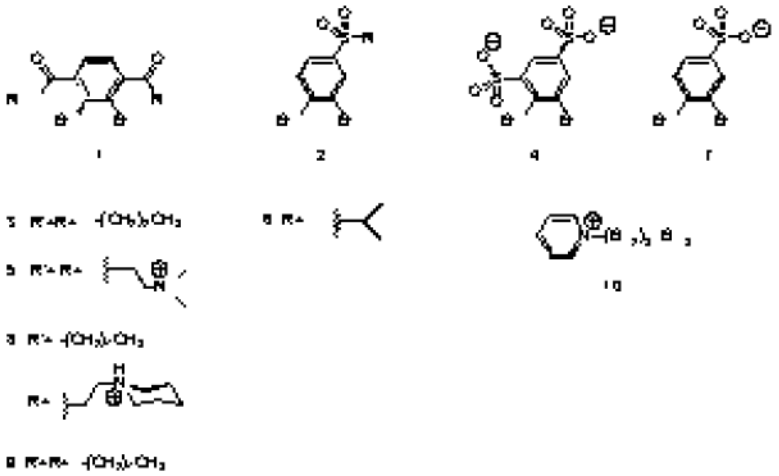


Figure 1. The structures of the catechol-based ligands discussed in this report.

Ligand synthesis. We have improved the synthesis of TAMs by developing a general procedure that avoids the protection and deprotection of the catecholate oxygens. This has streamlined the synthesis by reducing the synthetic steps from six to two. This procedure has also been extended to the synthesis of unsymmetrically substituted amides. Perhaps more importantly, the use of hazardous and expensive reagents used to install and remove the methyl protecting groups is avoided.

For the sulfonamide catecholates, a 3-step synthesis was developed that installs a single sulfonamide in the 4-position of the catecholate ring. A large number of bidentate ligands of this type have been synthesized, as well as tetra and hexa-dentate ligands. Progress has been made towards the synthesis of three other isomers: the 3-sulfonamide catecholate, the 3,5-disulfonamide catecholate (the sulfonamide of **4**), and the 3,6-sulfonamide catecholate (analogous to TAM).

Solution Thermodynamic Measurements. The protonation constants and Th(IV) and Fe(III) stability constants were determined for DMETAM **5** and 3,4-dihydroxy-benzene-*i*-propyl sulfonamide **6**. These numbers are summarized in the table below and the constants for **3**, **4** and **7** are included for comparison.

	PTAM **3** [1]	DMETAM **5**	i-PrSFAM **6**	**4** [4]	**7** [5]
pKa1	6.0	5.4	7.6	8.3	8.4
pKa2	11.0	10.95	11.9	12.0	12.5
β_{130} FeL3 [3]	43.1	45.68	43.3	46.3	40.1
pM [2]	22.8	25.83	19.5	20.7	13.7
β_{140} ThL4 [3]	——	47.52	52.6	——	——
pM [2]	——	19.9	19.0	——	——

Table 1. Summary of the protonation constants and Fe(III) and Th(IV) stability constants determined for the ligands **5** and **6** and comparison with known values for ligands **3**,**4**, and **7**.

5 was investigated because it is highly water soluble and more acidic than **3**. The increased acidity translates into higher pM values for the Fe(III) and Th(IV) complexes than any other ligand. It is remarkable that the addition of one sulfonamide group to the catechol ring has a greater electron withdrawing effect on the catecholate protons than two sulfonate groups; however, this is not mirrored in the Fe(III) formation constants. Since **6** has higher formation constants with Fe(III) than the **7**, we expect that bis-sulfonamides will have Fe(III) formation constants that are higher than the Fe(III) complex of **4**.

Extraction studies. We are currently examining some of these ligands as liquid-liquid extractants. Unfortunately TAMs and SFAMs form anionic metal complexes that are recalcitrant to organic extraction. By incorporating a positively charge substituent into one of the ligand side arms, the overall charge on the ligand will be -1, resulting in neutral metal complexes. Variations of both amide substituents are currently being evaluated for metal ion extraction.

It was necessary to evaluate the extraction using a competing ligand (NTA) for several reasons. We expect the ligands to function best at pHs above 5, so a water soluble ligand was required to prevent $Fe(OH)_3$ precipitation. Secondly, because the stability constants of the TAMs with Fe(III) are high and we expect the distribution coefficients to also be high, we want to maintain conditions where the metal is not 100% extracted. This allows for a more accurate determination of distribution coefficients and extraction constants. The extraction experiment is conducted with a buffered aqueous phase and a range of ligand concentrations. The amount of Fe(III) in the organic phase is monitored by UV-Vis spectroscopy.

The ligand **8** was found to be an excellent extractant at pH 5 using $CHCl_3$ as the extracting solvent. The distribution coefficients range from 10^{10} to 10^{12} for ligand stoichiometry ranging from 2 to 5 mole equivalents. As expected, a plot of Log D vs. Log [L] gave a straight line with a slope of approximately 3, the stoichiometry of the extracted species. The 3:1 L:Fe stoichiometry was also confirmed by the UV-Vis spectra and mass spectrometry of the organic phase. From this plot, the extraction constant was determined to be 10^{22}.

We also discovered that the symmetrical highly lipophilic ligand **9** would extract Fe(III) into ethyl acetate if a suitably lipophilic counter cation, cetyl pyridinium **10**, was used. Again, the distribution coefficients range from 10^{10} to 10^{11} for 2 to 5 molar equivalents of ligand. However, due to the large number of components that can constitute the extracted complex, we have not conclusively determined the species distribution in this system. This system is quite promising as an industrial extraction process because the ligands are inexpensive and efficiently synthesized and the cations are also inexpensive and commercially available. Qualitative experiments have shown that this extraction procedure is permissive to a variety of TAMs and SFAMs.

Planned Activities

In the area of solution thermodynamics, the Ce(IV) and ultimately Pu(IV) stability constants will be determined. The complexes will be structurally characterized. For the extraction studies, we will try to functionalize the TAMs to improve the solubility in industrially useful extraction solvents such as kerosene. The ion pair extraction system will be further characterized and our panel of previously synthesized ligands will be examined. Th(IV) extraction experiments are currently underway and Pu(IV) extraction experiments will begin this summer.

Information Access

1) Garrett, Miller, and Raymond. *Inorg. Chem.*, 1988, *28*, 128-133.
2) pM = -log $[M^{n+}]$ at pH 7.4 and $[M^{n+}]$ = 0.1mM and [L] = 1.0mM
3) $\beta_n = [ML_n] / [M^{n+}][L^{2-}]^n$
4) Shridah and Ohzeki. *Analyst*, 1986, *111*, 197.
5) Murakami, Nakamura. *Bull. Chem. Soc. Jpn.*, 1963, *36*, 1408